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Contributions from the Chemical Laboratory of Case School of Applied Science.

XX.—ON THE COMPOSITION OF THE OHIO AND CANADIAN SULPHUR PETROLEUMS.[1]

BY CHARLES F. MABERY.

Notwithstanding the great number of investigations that have been undertaken on petroleums from different countries, our knowledge of their composition, especially of the portions with high boiling-points, is still incomplete. What is known concerning American petroleums is based chiefly on the results of investigations which were carried on thirty years ago, before the discovery of several series of organic compounds, since shown to be contained in certain petroleums. With these facts in view, and having found in the study of the sulphur compounds from Ohio and Canadian petroleums that these oils are in certain respects peculiar in their composition, I have undertaken a comprehensive examination of them with reference to the different series of products which they may be found to contain. The study of Ohio petroleum seemed especially inviting on account of its origin in the Trenton limestone, a new horizon for a prolific oil supply, and its association with animal remains in the oldest geological formations of the continent. A similar interest attaches to the Canadian

[1] Presented to the American Academy of Arts and Sciences, October, 1894. Aid in the work described in this paper was given by the Academy from the C. M. Warren Fund for Chemical Research.

petroleum from the Corniferous limestone, which has yielded since 1862 enormous quantities of oil within the limited areas, less than thirty square miles, at Petrolia and Oil Springs. From the information already acquired concerning the nature of the sulphur petroleums, they seem to possess, beside their distinctive characteristics due to sulphur constituents, qualities of other petroleums which differ essentially in their composition.

In the earlier attempts to ascertain the constituents of petroleum, the methods then employed for fractional distillation were so inadequate that very little was accomplished. In 1862 the first systematic examination of American petroleum was undertaken by Pelouze and Cahours,[1] who showed the presence of the series of hydrocarbons C_nH_{2n+2}, beginning with butane. On account of a want of suitable apparatus for fractional distillation, their results lacked precision, and the questionable assumption was based upon them that petroleum is composed principally, including the heavier oils and paraffin, of the homologues of marsh gas. In accordance with the suggestion of Watts, these bodies were called the paraffin hydrocarbons, and as such they have since been known in chemical literature. Having obtained from coal-oil a series of hydrocarbons corresponding to certain members of the series discovered by Pelouze and Cahours, Schorlemmer[2] submitted the more volatile portions of American petroleum to distillation, and succeeded in separating hydrocarbons that had not been recognized by Pelouze and Cahours. In a more thorough and carefully conducted examination of Pennsylvania petroleum, carried on contemporaneously with the investigations of the chemists mentioned above, by means of an efficient fractional condenser devised especially for this and other similar investigations, C. M. Warren[3] avoided the errors of other experimenters and established beyond question the presence in Pennsylvania oil of two series of hydrocarbons, each with an homologous difference in boiling-points for CH_2 of 30°, and each member of one series differing in boiling-point from the isomeric member of the other series by a little less

[1] Compt. Rend., **54**, 1241; **56**, 505; **57**, 62.
[2] J. Chem. Soc., **15**, 419, (1862).
[3] Mem. Amer. Acad. (N. S.) **9**, 135; Proc. Amer. Acad., **27**, 56.

than 8°. One of the series C_nH_{2n+2} identified by Warren terminates at 127°.6, the other at 150°, the fractions of higher boiling-points containing members of the series C_nH_{2n}. The assumption of Pelouze and Cahours that the fractions with higher boiling-points have the composition represented by the general formula C_nH_{2n+2} was shown to be erroneous by the results of Warren, which excluded members of this series above 151°.

The presence of aromatic hydrocarbons in American petroleum was first recognized by Schorlemmer in 1865. Pelouze and Cahours had previously stated that American petroleum contained no aromatic hydrocarbons, but Schorlemmer collected a distillate from Canadian petroleum below 150°, and upon treating it with nitric acid and reducing with tin and hydrochloric acid, after distillation he obtained an oil with an odor of aniline that gave, with bleaching powder, the rosaniline reaction. The portion distilling between 150° and 170° gave a mixture of solid and liquid nitro-products, and the solid portion proved to be trinitrocumol. Benzol and its homologues were also found by Schorlemmer in Pennsylvania petroleum, in Galician petroleum by Freund[1] and others, and in Hanover petroleum by Bussenius and Einstuck.[2] In Galician petroleum Pawlewski[3] found two per cent. of aromatic hydrocarbons, chiefly benzol and paraxylol, the latter never having previously been recognized in any petroleum. In the fraction 170°–190° from American kerosene, Engler[4] discovered pseudocumol and mesitylene by the formation of nitro-compounds, and calculating the weight of crude oil corresponding to the weight of kerosene taken, it was estimated that these constituents are contained in crude Pennsylvania oil to the extent of 0.2 per cent. These hydrocarbons were also found in German, Galician, Italian, and Russian petroleum, in the latter to the extent of 0.1 per cent. According to the results of Beilstein and Kurbatoff,[5] the petroleum of the Central Caucasus has an essentially different composition from that of the deposits on the coast of the Caspian Sea. Oil obtained from the region of Zarskige Kolodzy, in the precinct of

[1] Ann. Chem. (Liebig) **115**, 19. [2] *Ibid.*, **113**, 151.
[3] Ber. d. Chem. Ges., **18**, 1915. [4] *Ibid.*, **18**, 2234.
[5] *Ibid.*, **13**, 1818; **14**, 1620.

Tiflis in the Central Caucasus, proved to contain small amounts of benzol and toluol, but to consist principally, like the Pennsylvania petroleum, of the series C_nH_{2n+2}. Pentane, hexane, and heptane were identified. The oil from Baku on the coast contains the series C_nH_{2n+2} in smaller quantity, and Beilstein and Kurbatoff found no trace of the aromatic hydrocarbons C_nH_{2n-6}, but the principal constituents are members of the series C_nH_{2n}. In Pennsylvania petroleum, Beilstein and Kurbatoff[1] recognized hexahydroisoxylol. In the fraction 95°–100° the same chemists detected the presence of a body containing less hydrogen than is required for the series C_nH_{2n+2}. Crude American heptane, when treated with nitric acid, gave a nitro-product corresponding to the formula $C_7H_{15}NO_2$. Nearly coincident with the researches of Beilstein and Kurbatoff, Schützenberger and Jonine[2] identified in the petroleum of Baku, hexahydrobenzol and hexahydrotoluol.

In their classic researches on the composition of the Caucasus petroleum, Markownikoff and Ogloblin[3] showed the presence in the oil from Baku, of benzol, toluol, isoxylol, pseudocumol, mesitylene, isodurol, durol, and higher hydrocarbons of the composition $C_{11}H_{14}$, $C_{12}H_{14}$, $C_{11}H_{12}$, and $C_{13}H_{14}$, and others, possibly homologues of styrol and phenylacetylene. Contrary to the experience of others, Markownikoff and Ogloblin found the naphtha from the Balachany plain on the Apscheron peninsula very rich in aromatic hydrocarbons; in the oil from the Central Caucasus, naphtenes were found to the extent of 80 per cent., and the aromatic hydrocarbons C_nH_{2n-6} to the extent of 10 per cent. At first Markownikoff looked upon the naphtenes as isomeric with the hexahydrocompounds, but later Markownikoff and Spady[4] appear to accept the identity of octonaphtene and hexahydroisoxylol.[5] As members of the naphtene series C_nH_{2n}, Markownikoff and Ogloblin identified hexahydromesitylene and the higher homologues between C_9H_{18} and $C_{15}H_{30}$. In petroleum from Boryslaw in Galicia, beside benzol, toluol, isoxylol, and

[1] Ber. d. Chem. Ges., **13**, 2028. [2] Compt. Rend., **91**, 823.
[3] Ann. chim. phys., [6], 372. [4] Ber. d. chem. Ges., **20**, 1850.
[5] In the *Berichte* (No. 7, April, 1895), recently received, the synthesis of 1-3-dimethylhexamethylene, $C_6H_{10}(CH_3)_2$ is described by Zelinsky, and it is shown to be identical with the octonaphtene of Markownikoff, or hexahydroisoxylol.

mesitylene, Lachowicz[1] found of the hexahydro series only hexahydroisoxylol.

The presence of unsaturated hydrocarbons C_nH_n in American petroleum was not mentioned in the early publications of Pelouze and Cahours, nor were they referred to by Schorlemmer. Warren[2] separated from Pennsylvania petroleum, rutylene, $C_{10}H_{20}$, boiling-point 174°.9; margarylene, $C_{11}H_{22}$, boiling-point 195°.8; and laurylene, $C_{12}H_{24}$, boiling-point 216°.2. In an examination of a hydrocarbon naphtha obtained as a product of the destructive distillation of a lime soap prepared from menhaden oil, Warren and Storer[3] discovered the series C_nH_{2n+2}, beginning with C_6H_{14}; members of the aromatic series, including benzol, toluol, xylol, and isocumol; and a series of the general formula C_nH_{2n}, as follows; rutylene, $C_{10}H_{20}$; margarylene, $C_{11}H_{22}$; laurylene, $C_{12}H_{24}$; identical with the hydrocarbons previously separated by Warren from Pennsylvania petroleum. Warren and Storer also submitted Rangoon petroleum to prolonged distillation, and they succeeded in proving the presence in this oil of rutylene, margarylene, laurylene, cocinylene, and naphthalene.

As early as 1842, Pelletier and Walther separated a hydrocardon from the "steinöl" of Amiano boiling at 80–88°, to which they assigned the formula C_7H_{14}. A similar product with the properties of heptylene was obtained by Mabery and Smith[4] as one of the products in the sulphuric-acid extract from the refining of Ohio burning-oil distillate.

More recently Engler[5] subjected menhaden oil to distillation under a pressure of ten atmospheres, and from the distillates thus obtained hydrocarbons were separated which proved to be identical with those contained in natural petroleum. These products included the light constituents of gasoline, the hydrocarbons of which burning-oil is composed, the heavy oils, and paraffin. Engler, therefore, believes in the origin of petroleum from the decomposition of animal remains. The hydrocarbons distilling above 160°, referred by Pelouze and Cahours to the series C_nH_{2n+2}, may really be

[1] Ann. Chem. (Liebig), **220**, 187.
[2] Proc. Am. Acad., **27**, 56; communicated May 12, 1868.
[3] Mem. Amer. Acad. (N. S.), **9**, 177. [4] Proc. Am. Acad., **25**, 222.
[5] Ber. d. chem. Ges., **21**, 1816.

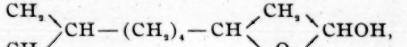
naphtenes or similar bodies. In most petroleum most recently examined, it is believed that the unsaturated hydrocarbons are not present in the crude oil, but when found in the products of distillation have resulted from decomposition. Beilstein and Kurbatoff stated that the series C_nH_{2n} in the Caucasus petroleum does not consist of the homologues of ethylene. In the lower fractions of Galician oil, Lachowicz obtained no reaction with bromine even after long standing. Above 200° the ready absorption of bromine indicated the presence of unsaturated hydrocarbons; but it was attributed to decomposition. On the other hand, Engler[1] found that petroleums from Pechelbronn (Alsace), Oelheim (Hanover), Tegernsee, Pennsylvania, Galicia, and Baku contain members of the series C_nH_{2n+2} and C_nH_{2n}, both unsaturated hydrocarbons and naphtenes. Engler asserts that all petroleums have the same composition, differing only in the proportions of their constituents. Markownikoff and Ogloblin[2] suggest the presence of unsaturated aromatic hydrocarbons in the oil from Baku.

Most analyses of crude petroleum have fallen short of 100 per cent., and the deficiency has been attributed to the presence of oxygen. In ascertaining the composition of oils from different districts, St. Claire Deville[3] showed that the percentage of oxygen varies between 2.1 per cent. in the Canadian petroleum and 5.6 per cent. in the oil from Zante. In 1874, Hell and Medinger[4] attempted to separate acids from crude petroleum by agitating it with a solution of sodic hydrate and precipitating with sulphuric acid. The oil which separated was distilled and converted into a methyl ether. By saponification of this ether an acid was obtained to which was assigned provisionally the formula $C_{11}H_{20}O_2$. From the sodic hydrate solution used in the refining of Baku oil, by the addition of sulphuric acid, Aschan[5] separated a mixture of acids, and, taking advantage of a difference in solubility of their salts, he obtained one acid, $C_9H_{14}O_2$, distilling at 237–239°, and another, $C_9H_{16}O_2$, that distilled at 251–253°. The first acid, called by Aschan octonaphtenecarboxylic acid, by dis-

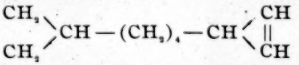
[1] Ztschr. angew. Chem., 1888, p. 73. [2] Ber. d. chem. Ges., **16**, 1873.
[3] Compt. rend., **66**, 442; **68**, 485. [4] Ber. d. chem. Ges., **7**, 1216.
[5] *Ibid*, **23**, 867; **24**, 1864, 2710: **25**, 3661.

tillation with hydriodic acid, was converted into hexahydro-isoxylol.

The oxygen compounds in petroleum were considered by Zaloziecki[1] to be lacto-alcohols which are oxidized to acids by contact with air. By the same method which was followed by Hell and Medinger, and Aschan, Zaloziecki obtained an acid, $C_{10}H_{18}O_3$, to which he gave the formula,



and to the hydrocarbon obtained by distillation with hydriodic acid he gave the formula,



Engler looks upon these acids as formed by oxidation of other constituents of the crude oil. According to the results of Markownikoff and Ogloblin,[2] the fraction 75–85° from Caucasus oil contains 0.76 per cent. of oxygen compounds, and the fraction 220–230°, 5.21 per cent. These oxygen compounds are in part acid, in part neutral, and in part phenol. The acids $C_{10}H_{19}COOH$ and $C_{11}H_{21}COOH$ were obtained as colorless oils; Markownikoff[3] and Ogloblin regarded these substances as naphtenecarboxylic acids.

Most petroleums have been shown by analysis to contain nitrogen, usually in minute quantities. In distillates from Pennsylvania oil, Beilby[4] found 0.08 per cent. in the residuum or tar, and 0.375 per cent. in the coke. Since the tar was one-tenth of the crude oil, the latter contained 0.008 per cent. of nitrogen. In crude Russian oil Beilby found 0.05 per cent. Peckham[5] found in West Virginia oil 0.54 per cent., in Mecca oil, 0.23 per cent., and in California oil, 0.56—1.1 per cent. of nitrogen. In Egyptian oil, Kast and Kunkler[6] reported 0.3 per cent. of nitrogen, 1.21 per cent. of sulphur, and 0.92 per cent of oxygen. Weller[7] detected certain alkaloid bases in paraffin oil, and Bandrowski[8] described a thick, transparent

[1] Ber. d. chem. Ges., **24**, 796, 1808. [2] Ann. chim. phys., [6], **2**, 372.
[3] Ber. d. chem Ges., **16**, 1873. [4] J. Soc. Chem. Ind., 1891, p. 120.
[5] Geological Survey of California, Appendix to Vol. **40**, 89.
[6] Chem. Centrbl., 1890. p. 932. [7] Ber. d. chem. Ges., **20**, 2097.
[8] Monatsh. Chem., **8**, 224.

liquid solidifying at 20°, which he obtained by agitating Galician oil during several weeks with sulphuric acid. This substance gave a platinum salt containing 19.7 per cent of platinum. Upon neutralizing a sulphuric acid extract obtained in refining with calcic hydrate and distilling with steam, Zaloziecki[1] obtained an oil containing nitrogen that formed a platosochloride whose percentage-composition corresponded with that of tetrahydrocoridine $(C_{10}H_{13}NCl)_2PtCl_4$, or to the formula $(C_{10}H_{21}NCl)_2PtCl_4$; another insoluble platoso compound was shown by analysis to have the composition represented either by the formula $(C_{10}H_{15}NCl)_2PtCl_4$ or $(C_{10}H_{17}NCl)_2PtCl_4$.

Several hydrocarbons have been described as occurring in the less volatile portions of American petroleum. Hemilian[2] obtained from the high boiling fractions "petrocene," a crystalline body melting above 300°. To this substance was assigned the formula $C_{25}H_{32}$. Prunier and David[3] stated that they had obtained evidence of the presence in refinery residues of anthracene, chrysene, pyrene, phenanthrene, chrysogene, retene, benzerythrene, fluoanthrene, parachrysene, paranthracene, an isomeric acenaphthylene, besides different paraffins and stilbene. In the "petrocene" and "carbopetrocene" prepared from the tarry residue of petroleum, Prunier and David identified compounds, the former melting at 160–190°, the latter at 200–238°, and also thallene melting at 110°. They attributed the green fluorescence in petroleum to the presence of quinones. Inasmuch as these products were obtained from the distillation of tar in coking, evidently no inference is permissible concerning their presence in the crude oil. From "petrocene," Sadtler and McCarter[4] separated two hydrocarbons, one of which melted at 280° and the other at 178°. From these hydrocarbons the quinones were prepared and from one an alizarin.

In undertaking an examination of the Ohio and Canadian sulphur oils with the advantage of former experience in studying the sulphur constituents, it was evidently necessary to conduct the distillations with all possible precautions to

[1] Monatsch. Chem., 13, 498. [2] Ber. d. chem. Ges., 9, 1604.
[3] Bull Soc. chim. (Paris) [2], 31, 158. [4] This JOURNAL, 1, 30.

avoid decomposition. The tendency of the sulphur oils to decomposition by heat is due as much at least to the action of air on the hot oil as to the increased temperature. Markownikoff and Ogloblin attributed the decomposition in the distillation of the Russian oil to polymerization of the unsaturated compounds, and perhaps also to the polymerization of certain aromatic compounds, such as phenylacetylene, and they found that coloration of distillates on standing was less marked when the oxygen compounds had been removed. This tendency towards polymerization in unsaturated hydrocarbons separated from sulphuric-acid solutions was observed by me,[1] and it will receive further attention. It was therefore deemed advisable to carry on all distillations from the crude oils, instead of relying upon refinery products, except only the most volatile distillates, and the advantage gained has been apparent in subsidiary distillations of refinery-oils which had been subjected to the decomposition incident to refinery-distillation. Longer time is then necessary for separations, and the odor of decomposition is retained indefinitely during subsequent distillations. Certain constituents of sulphur petroleums are even more unstable than the sulphides, as shown by the rapid coloration of the oils when distilled, even after removal of the sulphides by mercuric chloride. Nevertheless, in the separation of constituents requiring larger quantities of distillates than can conveniently be collected *in vacuo*, since only porcelain or earthenware stills are admissible on account of the decomposition in metallic stills, it may be necessary to depend to a limited extent upon refinery distillates.

After the first distillation of the crude oils *in vacuo*, distillation of the portion collected below 150° was continued under atmospheric pressure, since it occasioned no appreciable decomposition. Under the diminished pressure some loss of the constituents with low boiling-points could not be avoided; but this was not important, since refinery-distillates could be utilized for the separation of the volatile hydrocarbons. Distillation of considerable quantities of oil *in vacuo* presented certain difficulties. Neither glass nor metallic stills were suitable, and no American earthenware stills could be pro-

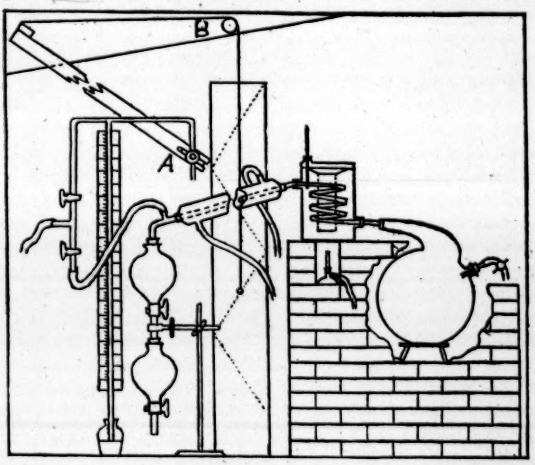
[1] This JOURNAL, 16, 92.

cured that would support a vacuum on account of porosity from imperfect molding and glazing. Some of the English earthenware has supported a vacuum, but the ideal stills for such work, or for any distillations in large quantities, when metals cannot be employed, are those manufactured in the Royal Berlin Porcelain Factory. We have had a three-gallon porcelain still and several others of smaller capacity in operation almost continuously during several months with apparently no deterioration. When these stills are enclosed within a brick chamber, the temperature of distillation may, without difficulty, be carried above 350° by means of large laboratory burners. Another serious obstacle immediately presented itself in the porosity of common corks, which alone could be used for connections. After much labor it was found that tight joints could be secured by means of a rubber lute made by dissolving gum rubber in very light gasoline. Thin films of this lute drawn by the inward pressure into the joints and imperfections in the corks, after several applications, formed sufficiently close connections. Any other than the lightest gasoline as a solvent leaves a sticky film that is unpleasant to manipulate.

An important feature in prolonged fractional distillations *in vacuo* is a simple and convenient means for maintaining, without too close attention, a constant tension within the still. Air must not come in contact with the hot oil or vapor, and it would require too large quantities of an inert gas. An expedient suggested itself in the fact that occasionally small leaks held the manometer column stationary at whatever height it happened to stand. It therefore seemed possible to graduate leaks apart from the still in such a manner that the tension could be held constant for some time at any desired point.

The accompanying figure represents the form of regulator that has been used in all our distillations of large as well as small quantities of oils, together with the complete apparatus in the form for use. The regulator consists simply of a glass stopcock, *A*, better of considerable size, attached to the manometer by means of a side tube. To regulate closely the inflow of air an arm three to five feet in length, according to the working of the stopcock, is attached firmly to the head of

the cock, and supported in a manner easily movable within very small divisions on the arc of a circle of which it is the radius. To enable the operator to make adjustments while standing in front of the manometer, a piece of lead is attached as a weight to the upper end of the lever, and a cord is carried over a pulley, *B*, and terminates in a ring in front of transverse rows of pins a few millimeters apart. For economy of space the pulley is placed lower in the figure than its actual



position. The upper part of the lever consists of two strips of wood, with a space between, through which passes a rigid copper wire as a support and guide. When the lever is in a vertical position, the stopcock is fully open ; any adjustment is easily obtained, and the manometer may be held stationary within one millimeter at any desired point during several hours.

In the distillation of small quantities of liquids, requiring constant attention, we have used a piece of glass tube 45–60 mm. long, attached to the side stopcock, with a sliding support near the end. In vacuum-distillations on a large scale it

is more convenient to refer to the entire length of the manometer column, since at any time leaks may occur that are indicated only on the lower portion of the graduated scale. With a short manometer column alone, much time may be lost in waiting for an exhaustion that is interfered with by leaks.

In heating the still, direct contact with the flame was prevented by maintaining an air space above the burner by means of a sheet of asbestos. With such application of heat equally on the sides and bottom, there was less danger of decomposition at high temperatures. All but the highest distillates were collected in a Warren hot condenser containing a glass worm. With this condenser vacuum-distillations are easily controlled, and, as in distillations under atmospheric pressure, with a great economy of time. Continuous distillation is possible without losing the vacuum, by drawing in consecutive fractions through the rear tubulure of the retort. The two receivers shown in the figure are convenient, and some additional advantage would be gained by means of an independent vacuum connection with the lower receiver. Several supports are not represented in the figure. Much time and tedious labor were expended on this apparatus before all the difficulties were overcome; but the compensation was ample, since by means of it we have been able to separate in considerable quantities constituents of high boiling-points without decomposition, which otherwise would have been impossible. As an evidence of its usefulness, during several months continuous distillations were in progress, in charge of assistants, with highly satisfactory results. Distillates were collected at intervals of 10°, 5°, and 2°. The depression in boiling-points by the diminished pressure in vacuum-distillation varies between 60° and 65° for the lower constituents, and 125° or more for those collected between 300° and 350°. The residue above 350° (450–500° atmospheric pressure) in both Ohio and Canada oils had apparently undergone but little decomposition; in appearance, it was a thick, ready-flowing oil, with scarcely any odor.

A portion of the residual oil above 350° *in vacuo* was redistilled in an ordinary boiling-flask, and the temperatures of the

vapor and of the liquid were read on a Mahlke 550° thermometer. The oil began to distil with much decomposition at 385° in the vapor, and 415° in the liquid. One-half distilled with the temperature in the liquid below 430°. Doubtless the temperatures of distillation were much reduced by the decomposition. Since we have found that distillations below 250° may be carried on successfully without serious decomposition in an atmosphere of carbonic dioxide, when we return to the distillation of the higher constituents this method may be serviceable.

Ohio Petroleum.

In the study of Ohio petroleum I have been aided by Mr. E. J. Hudson.[1] Besides the publications from this laboratory on the sulphur compounds[2] and those of Orton,[3] I am aware of no published statements concerning the composition of Ohio sulphur petroleum. The crude oil which formed the basis of our work was received from the Peerless Refining Company, Findlay, which controls a large section of oil territory. When received, it was of a somewhat thicker consistency than ordinary Pennsylvania oil, with a slight odor of hydric sulphide that is usually observed in crude sulphur oils. It contained a small quantity of water, which was removed completely only after long standing with fused calcic chloride. In determining the specific gravity of Ohio sulphur petroleums, oils were collected from wells at different points in the Findlay and Lima fields. The determinations were made at 20°.

Findlay Field.

	Specific gravity.
(1) Barnsville	0.8272
(2) Heilstone Oil Co., Well No. 2, Hancock County	0.8296
(3) Ohio Oil Co., Wood County	0.8194
(4) Langmade Well, No. 4, Portage, Hancock County	0.8149
(5) Peerless Refining Co., Well No. 2, Liberty, Hancock County	0.8278
(6) Peerless Refining Co., Well No. 5, Baltimore, Wood County	0.8239

[1] A part of this work formed the subject of a thesis by Mr. Hudson for the degree of Bachelor of Science.

[2] Proc. Am. Acad., **25**, 218; this Journal, **16**, 83.

[3] Ohio State Geological Reports, 1886, 1888, 1890; U. S. Geological Report, 1886-87.

Lima Field.

The following specimens of crude oil, representing different portions of the Lima and Findlay Fields, were received from the Ohio Oil Company, with a history of each well:

Township.	County.	Drilled.	Sand. Feet.	Oil. Feet.	Depth. Feet.	Production after shot. Daily.	Production at present. Daily.
(1) St. Mary's	Auglaize	May, 1872	1132	1147	1166	100 bbls.	5 bbls.
(2) Liberty	Hancock	Aug. 1893	1250	1273	1286	75 "	10 "
(3) Montgomery	Wood	Oct. 1892	1192	1197	1242	25 "	5 "
(4) Woodville	Sandusky	July 1892	1180	1195	1205	125 "	10 "
(5) Nottingham	Wells, Ind	April 1895	900	1004	1044	165 "	75 "
(6) Liberty	Wood	Sept. 1894	1152	1172	1227	125 "	30 "
(7) Lima	Allen						

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Sp. gr.	0.8288	0.8345	0.8265	0.8254	0.8243	0.8428	0.851

There is evidently an appreciable variation in the composition and properties of the oils from different points in the Ohio field. Marked differences occur in the specific gravity as well as in the percentages of carbon, hydrogen, nitrogen, and sulphur.

The oil that was employed in this examination was somewhat heavier, with a specific gravity 0.8380. These results show an appreciable variation even in different portions of the same field. A similar variation in specific gravity has been observed in other fields:

	Specific gravity.
Alsace (Pechelbronn), depth 146 feet (Engler)	0.906
" " " 213 " "	0.885
Oelheim (Hanover) "	0.889
Tegernsee "	0.815
Pennsylvania "	0.8185
" "	0.801
Galicia "	0.8235
Baku "	0.859
" "	0.810
Ohio (Mabery)	0.838
" (Markownikoff and Ogloblin)	0.887
Baku (Apscheron) " " "	0.855–0.885
Galicia " " "	0.835–0.895
American petroleum (Petrolitz)	0.830
" " (Weil)	0.827
Canada (Markownikoff and Ogloblin)	0.828
" " " "	0.844
Alsace (Pechelbronn) " " "	0.668

The value 0.887 assigned by Markownikoff to Ohio oil is much higher than has elsewhere been given. It must have been obtained in an oil from another Ohio field, perhaps from the Mecca district. The values given by Markownikoff for Canada oil must refer to a product from the Oil Springs district, although the number 0.828 is lower than is usually found even in that oil. The numbers given by Redwood are 0.844–0.854 for Oil Springs oil, and 0.859–0.877 for Petrolia oil. In Oil Springs oil we found 0.8427–0.8389 (gas oil), 0.8442, and in Petrolia oil, 0.8553, 0.8621, 0.8800.

In ascertaining the quantity of sulphur by combustion in air in the crude oil from which distillates were prepared for examination, the following results were obtained: (1) 0.73 per cent., (2) 0.72 per cent., (3) 0.72 per cent. In oils previously examined the percentage of sulphur has not been above 0.60. Sulphur was also determined in the oils collected in the Findlay and Lima districts in the order of the numbers given above:

	Findlay.	Lima and Findlay.		Findlay.	Lima and Findlay.
(1)	0.33	0.61	(5)	0.68	0.56
(2)	0.63	0.71	(6)	0.61	0.76
(3)	0.56	0.37	(7)		0.81
(4)	0.68	0.49			

In Apscheron oil, Markownikoff and Ogloblin[1] obtained 0.064 per cent., and 0.16 per cent. in Trans-Caspian oil.

The percentages of carbon and hydrogen in the oil from which distillates were obtained were found by combustion in air with a layer of plumbic peroxide in front to retain the sulphur[2]: carbon, 84.57; hydrogen, 13.62. In other samples from Findlay and Lima carbon and hydrogen were also determined:

	Findlay.		Lima and Findlay.	
	C.	H.	C.	H.
(1)	85.76	13.56	84.73	13.48
(2)	85.82	13.80	84.03	13.05
(3)	84.33	13.46	83.89	13.18
(4)	84.35	13.36	84.55	13.55
(5)	84.20	13.41	83.41	13.13
(6)	84.18	14.60	85.07	13.33
(7)			85.00	13.05

[1] Ann. chim. phys. [6], **2**, 393.
[2] Warren: Proc. Am. Acad., **6**, 472.

The percentages of carbon and hydrogen that have been found in analyses of oils from other deposits are given in the following table:

	C.	H.	O.
Apscheron (Markownikoff and Ogloblin)	86.65	13.35	
" " " "	87.01	13.22	
" " " "	86.89	13.18	
Trans-Caspian " " "	86.75	12.19	
Egyptian (Kast and Kunkler)[1]	85.85	11.72	
Pechelbronn (Sainte-Claire Deville)[2]	85.7	12.00	2.3
Galicia (St. Claire Deville)[2]	82.2	12.10	5.7
Rangoon (St. Claire Deville)[2]	83.8	12.7	3.5

The following values represent the percentages of carbon and hydrogen in crude petroleum from other American oil fields:

	C.	H.	O.
W. Virginia, Scioto Well (Peckham)[3]	86.62	12.93	
W. Virginia, Cumberland Well (Peckman)[3]		13.38	
California oil (Peckman)[3]		11.82	
Mecca oil (Peckham)[3]	86.32	13.07	
Canada, Manitoulin (Deville)[2]	83.00	14.6	2.4
" Petrolia "	84.5	13.5	2.0
" West "	79.4	14.1	6.5
Ohio oil "	84.2	13.1	2.7
Pennsylvania oil "	83.4	14.7	1.9
" " "	84.19	13.7	1.4

In the crude oil used in this examination, and in the other specimens described above, nitrogen was determined by the Kjeldahl method, and several closely concordant results were obtained by combustion with soda-lime; the former gave 0.11 per cent., and the other oils the following percentages:

Findlay.	Lima and Findlay.
(1) 0.26 per cent.	0.068
(2) (*a*) 0.023, (*b*) 0.023 per cent.	0.047
(3) 0.21 per cent.	0.054
(4) 0.13 "	0.049
(5) 0.35 "	0.060
(6) 0.08 "	0.056
(7)	0.024

The presence of nitrogen in Ohio and Canadian petroleum

[1] Chem. Centrbl., 1890, p. 932.
[2] Compt. rend., **68**, 485.
[3] Geological Survey of California, II, Appendix, p. 39.

will receive further attention at the close of this paper in some observations on the origin of petroleum.

The bromine absorption in the crude oils was determined by the method described in Allen's "Commercial Organic Analysis." A weighed quantity of the oil was allowed to stand in the dark with a slight excess of bromine dissolved in dry carbonic disulphide, and the portion not absorbed was titrated with standard solutions of sodic hyposulphite and iodine. The strength of the bromine solution was ascertained by parallel titrations. Approximately one per cent. of hydrobromic acid is evolved in these determinations in crude oils.

	Findlay.	Lima and Findlay.		Findlay.	Lima and Findlay.
(1)	11.29	8.74	(5)	13.07	10.93
(2)	14.62	9.31	(6)	11.32	12.31
(3)	10.55	11.49	(7)		12.06
(4)	14.89	12.30			

A comparison of the bromine-absorption of the sulphur oils with that of oils from other sources indicates that bromine-absorption is independent of sulphur compounds, and a distinctive property of petroleums in general. The following determinations were made:

Chinese petroleum	10.90 per cent.
Italian petroleum	7.10 "
Macksburg, O., petroleum	9.74 "
Berea Grit, O., petroleum	10.71 "
California petroleum	9.88 "

The quantities of bromine absorbed by distillates from the crude sulphur oil were also determined:

Fractions.	Percentage of bromine absorbed.
110–150°	0.73
150–220°	1.74
220–257°	4.84
257–300°	5.04
300–330°	12.10
Residue	19.50

Throughout this investigation some reliance has been placed on the absorptive capacity for bromine of crude oils and distillates obtained from them as indicating a certain unsaturated condition. While it should be borne in mind that a considerable proportion of the bromine-absorption is due to

the sulphur constituents, there is besides a large absorption in the crude oils and in the residues of distillation above 350° by other constituents. There is much yet to be learned concerning the decompositions in distillations at high temperatures, which are indicated by the greatly increased bromine-absorption, and the study of the higher-boiling portions will be greatly facilitated by the aid of the Mahlke thermometers for observing temperatures below 550°.

The characteristic qualities of Ohio oil appear also in the proportions that distil at different temperatures; 800 grams of the crude oil collected in the following proportions beginning at 110°:

	110–150°.	150–220°.	220–257°.	257–300°.	300–350°.	Residue.
Grams	76	133	86	76	69	348
Percentage	9.75	16.63	10.75	9.75	8.63	43.5
Sp. gr. at 20°	0.7282	0.7669	0.7940	0.8138	0.8242	0.8976
Per cent. sulphur	0.10	0.38	0.41	0.36	0.37	0.54

The distillates below 235° were colorless, and no odors resulting from decomposition were observed. Above this point color appeared in the distillates, with the odor of decomposition, which became more marked with increasing temperatures. Above 275° the heavier paraffin-oils began to distil. In refinery-distillation of Ohio petroleum it is therefore evident that cracking begins in the vicinity of 250°. No doubt crude sulphur petroleums undergo decomposition spontaneously to some extent, since upon standing they always contain hydric sulphide. We find that certain unstable constituents separated from the crude oils gradually become darker in color, with other indications of chemical change. At the beginning of the distillation hydric sulphide came off in considerable quantities, but after the first fraction very little appeared in the succeeding distillates below the point where decomposition began.

On account of the viscous character of the Ohio and Canadian petroleums and the large proportion of heavy oils, temperatures indicated by the thermometer in the vapor of the distillates should be higher than the corresponding temperatures of the oil. To ascertain this difference, crude Findlay oil was distilled, and the temperature of the distillates and of the oil were noted with the following results:

Thermometer in the oil.	Thermometer in the vapor.	Difference.
167°	120°	47°
180°	140°	40°
203°	160°	43°
221°	180°	41°
238°	200°	38°
259°	220°	39°
282°	240°	42°
301°	260°	41°
318°	280°	38°
341°	300°	41°

Except in the first reading the average difference in temperature is about 40°.

Determinations of sulphur in the crude oil and in the distillates obtained from it, showed that considerable sulphur was lost during distillation. In order to obtain definite information concerning the quantity lost, 100 grams of the crude oil were distilled under atmospheric pressure, and attached to the receiver were flasks containing a solution of sodic hydrate for the purpose of absorbing any hydric sulphide that escaped. In front of the flask containing hydric sulphide there was connected another flask, which contained alcohol, with a delivery tube in front to absorb volatile products that might result from decomposition. The oil was fractioned to 300°, collecting between 115° and 250°, and between 250° and 300°, and the hydric sulphide was determined after oxidation with bromine by precipitation with baric chloride. The percentage of sulphur in the several fractions was also determined. As usual in distillation of the sulphur petroleums, a slight sublimate of sulphur was observed in the neck of the condenser. Upon diluting the alcohol it became slightly turbid, which indicated probably some volatilization of sulphur constituents. The alkaline solution of the sulphur from the distillate 115–250° gave 0.1135 gram of baric sulphate, corresponding to 0.0156 gram of sulphur. From the alkaline solution of the sulphur absorbed from the fraction 250–300°, 0.6946 gram of baric sulphate was obtained, corresponding to 0.0958 gram of sulphur. A determination of sulphur in the distillate 115–250° gave 0.55 per cent.; in the distillate 250–300°, 0.51 per cent; and in the residue above 300°,

0.60 per cent. Since the weight of the distillate collected at 115–250° was 20.55 grams, the weight at 250–300°, 5.1 grams, and the weight of the residue above 300°, 74.35 grams, the total weight of sulphur accounted for in these determinations was 0.7166 gram, leaving 0.27 gram which must have escaped in ways not determined.

In comparing the quantities of the distillates from Ohio oil, and their specific gravities, with those obtained by Markownikoff and Ogloblin[1] in the Apscheron oil with a specific gravity at 17° of 0.882, and those given by Bolley from Pennsylvania petroleums with a specific gravity of 0.816, it is evident that the properties of Ohio petroleum place it between the Caucasus and Pennsylvania oils.

The Caucasus oil began to distil at 120° in the vapor, and 180° in the liquid.

Apscheron.			Pennsylvania.			Ohio.		
	Parts in 100.	Sp. Gr.	Parts in 100.	Sp. Gr.		Parts in 100.	Sp. Gr.
120–150°	0.5	0.786	19.70		110–150°	9.75	0.7282
150–200°	10.9	0.824	8.84	0.757	150–220°	16.63	0.7669
200–250°	12.8	0.861	15.23	0.788	220–257°	10.75	0.7940
250–320°	24.7		20.7	0.809	257–300°	9.75	0.8138
					300–350°	8.63	0.8242
Total	48.9		64.48			55.51	
Residue	52.1		35.52			43.00	

While the temperatures at which the Ohio oil was collected are slightly different from the others, they are sufficiently close for comparison.

Kramer[2] has compared the quantities of distillates obtained from crude petroleum of other fields:

	Sp. Gr.	—150°	150-250°	250-300°	Residue
Tegernsee	0.812	20.04	26.12	14.00	35.91
Pennsylvania	0.814	14.34	25.35	13.75	40.99
Baku	0.880	0.63	12.73	15.55	37.95
Oelheim	0.885	0.74	11.05	9.75	75.71
Alsace	0.888	1.3	16.37	17.07	47.88

Taubes Barlâdu[3] distilled 1115 cc. of crude Roumanian petroleum from the deposits on the south slope of the Car-

[1] Ber. d. chem. Ges., 16, 1873. [2] Chem. Centrbl., 1887, p. 290.
[3] Ztschr. ang. Chem., 1889, p. 606.

pathians, which are probably connected with the Galician oil zone, with the following results:

	cc.	Per cent. by volume.
30–125°	150	13.5
125–225°	385	35.5
225–280°	160	14.3
280–315°	98	8.1

In an examination of Burmese petroleum, Romanis[1] obtained an oil from Yay-nan-Chaung with a specific gravity of 0.8590, which solidified at 24°. An oil from Arracan with a specific gravity of 0.825 at 32° contained considerable benzol and other aromatic hydrocarbons. Upon distillation, the following results were obtained:

	Per cent.	Distilled with steam.	
			Per cent.
70–90°	3.1		
90–100°	7.6	—100°	23.3
100–130°	10.6	100–110°	33.0
130–200°	18.7	110–130°	29.3
200–300°	18.7	Residue	13.3 (heavy oil)
+300°	12.5		98.9
Oil in residue	8.0		
Paraffin	3.1		
Loss	17.7		
	100.00		

Markownikoff and Ogloblin examined the ash of Caucasus petroleum by igniting the residue of distillation. They found 0.09 per cent. of ash calculated for the original quantity of crude oil, and it consisted chiefly of the oxides of calcium, iron, and aluminum. Traces of copper and silver were also found. We have determined by combustion in oxygen the percentages of carbon and hydrogen in coke from the refinery residue of the distillation of Ohio petroleum; the percentage of carbon was 95.06, and that of hydrogen 4.85. A determination of nitrogen by the Kjeldahl method gave 0.31 per cent. The quantity of ash in the coke was determined by burning off the carbon, and the weight of ash thus obtained corresponded to 0.11 per cent. of the coke burned. In attempting to estimate the percentage of ash in the crude oil from the amount found in the coke, there is some uncertainty as to

[1] Chem. News, **59**, 292.

the quantity of oil corresponding to the coke. In some oils the proportion of residue is estimated at ten per cent. of the crude oil. It depends also upon the method followed by the refiner. Sometimes the first distillation of the crude oil is pushed to the point of complete decomposition, and the tar distillate is again distilled until it is coked. It is well known that earthy matter frequently remains for some time in suspension in the crude oil after it is taken from the wells. On this account, if the oil were distilled before the suspended material had subsided, the ash would not represent what had been in solution in the oil. But the oil is usually allowed to stand some time before distillation, and that the coke we examined was practically free from suspended matter is evident from the low percentage of ash, and corresponding results with Canadian oil where the ash was determined in a tar distillate and in coke from crude oil; the percentages of ash from the two sources were not very different.[1]

In Findlay oil, in which our determination was made, the proportion of still-residue is doubtless somewhat smaller than that mentioned above, probably between ten and five per cent. The corresponding percentage of ash in the crude oil would, therefore, be not far from 0.005, an amount considerably less than Markownikoff and Ogloblin found in Russian oil.

An analysis of the ash showed that it was composed chiefly of lime and magnesia, and the quantity of magnesia is at least equal to that of the lime. Traces of iron and aluminum were found, the iron possibly having been dissolved from the still. It is therefore evident that the crude oil has exerted an appreciable solvent action on the limestone reservoir, dissolving both constituents of the dolomitic rock.

It is maintained by some chemists that all petroleums contain the same series of compounds in different proportions, and that the difference in properties depends upon a variation in the quantities of the constituents. In a general sense, with respect to the principal series of hydrocarbons, this is doubtless true; yet there is such a wide difference in the properties of oils like those from Pennsylvania and the Caucasus that they are characteristic of substances quite unlike. The

[1] *Vide* Determination of Ash in Canadian Petroleum; second part of this paper.

Caucasus petroleum is wholly, or nearly, wanting in the series $C_n H_{2n+2}$, and the Pennsylvania oil evidently contains the series $C_n H_{2n}$ in much smaller proportion than the Russian oil. The presence of the higher members of the latter series in the Pennsylvania oil has yet to be ascertained. It is conceivable that the difference in the composition of petroleums is due to the different influences to which they have been exposed. Perhaps greater porosity of the reservoir or cover where oils exist under pressure has permitted an escape from certain oils of the more volatile constituents, especially of the series $C_n H_{2n+2}$. If this should be demonstrated by more extended observations, it would be reasonable to expect the same bodies in the Pennsylvania as in the Russian oil, only in smaller quantities of the higher constituents. Referring the sulphur in Ohio petroleums to the average composition of the compounds containing it, the crude oil should contain at least 5 per cent. of the sulphur derivatives. Evidently such a large proportion of the sulphur compounds in petroleum must exert an important influence on its properties, and we should therefore expect a marked difference between the sulphur petroleums and those which contain only traces of sulphur.

From a general similarity of Ohio petroleum to the oil from Pennsylvania, so far as it relates to hydrocarbons of the series $C_n H_{2n+2}$, it should perhaps be expected that the composition of the latter oil, which has been established beyond question, at least so far as the portions of low boiling-points are concerned, should represent also similar portions of the Ohio products. As mentioned above, even a casual examination of the sulphur oils affords abundant evidence that their peculiar properties depend upon other constituents than the hydrocarbons $C_n H_{2n+2}$. While these unique constituents may detract from, rather than enhance, the value of the sulphur oils for commercial purposes, it is as important for the intelligent guidance of the refiner as it is interesting from a scientific point of view that they be well understood.

While occupied with the sulphur compounds in Ohio petroleum, I was impressed with the complexity in composition manifested by the products of distillation, and with the importance of a thorough examination for all constituents. We

therefore began with an endeavor to separate and identify the individual homologues of methane which have been found in Pennsylvania petroleum, including an approximate quantitative determination of all but the more volatile members.

HYDROCARBONS C_nH_{2n+2}.

To separate the hydrocarbons of lower boiling-points we obtained 25 liters of the very first distillate from a 300-barrel still. This distillate contained 0.10 per cent. of sulphur. Considerable gas always escapes in refinery-distillation before a liquid distillate appears, but we have not yet undertaken an examination of its composition. Probably this is essentially the same as that of the gas given off in beginning a distillation of Pennsylvania oil together with hydric sulphide, which is always evolved to a greater or less extent in the distillation of sulphur petroleums. Sadtler[1] found that the gas from Pennsylvania wells consisted principally of methane, with some ethane, nitrogen, and hydrogen. In the gas from Canada wells, at Enniskillen, Fouquè[2] found marsh gas, ethane, and small quantities of carbonic dioxide. According to Ronalds,[3] the gas from Pennsylvania petroleum contains 1.27 per cent. of carbonic dioxide, 6.58 per cent. of oxygen, 54.00 per cent. of nitrogen, and 38.15 per cent. of ethane and propane; by exposing the escaping gas to a freezing-mixture, butane was condensed to a liquid.

In an exhaustive study of natural gas from Pennsylvania wells, Phillips[4] found that the principal constituents were hydrocarbons C_nH_{2n+2}, with nitrogen in variable proportions and carbonic dioxide in small quantity, but no hydrogen nor carbonic oxide.

The crude distillate was subjected to fractional distillation in a porcelain still, to which was attached a Warren condenser filled with a mixture of salt and ice, with ice alone, or with water, according to the fractions collected. Another ordinary condensing-worm surrounded with a freezing-mixture was placed in front. Subsequent distillations were conducted in glass stills, and the fractions rapidly accumulated within limits of temperature which distinguish the hydrocarbons C_nH_{2n+2}.

[1] Am. Chemist, 1876, p. 97.
[2] Compt. Rend., 67, 1045.
[3] J. Chem. Soc., 18, 54.
[4] This JOURNAL, 16, 406.

At the beginning of the first and second distillations, a delivery-tube was attached to the bottle receiving the distillate, and extended so as to collect in a receiver inverted over water any volatile constituents that might have escaped condensation. At first a very little gas collected, which burned with a smoky flame, but none afterwards. The following quantities were collected during the first distillation:

	—25°	25–30°	30–35°	35–40°
Grams	525	400	450	400

After the fourth distillation 35 grams collected between 0° and 1°, distilling for the most part at 0°, barometer 740 mm. This was evidently butane, boiling-point 0°. Inasmuch as the boiling-point of this hydrocarbon has been carefully determined,[1] further examination was not deemed necessary. The temperature rose rapidly to 5°, and, between 7° and 9°, 20 grams of a distillate collected, mostly between 7° and 8°, the boiling-point of a hydrocarbon which was separated by Warren from Pennsylvania petroleum, and which was regarded by him as one of the butanes. Since the atmospheric temperature was in the vicinity of 30° when these distillations were in progress, special care was necessary to preserve the distillates, and the ice accidentally becoming exhausted in the ice-chest, the distillate collected at 0° burst the bottle, and the one at 8° forced out the stopper and volatilized. Of the two possible butanes, the boiling-point of one is without question 0°. The other seems to have been obtained by Butlerow[2] from isobutyl alcohol, and the boiling-point assigned to it was —17°.5. Under more favorable conditions, we shall collect a larger quantity of this distillate, to determine by its chemical behavior, as well as by its constancy in boiling-point, whether it be a definite compound.[3]

[1] Ronalds: J. Chem. Soc., **18**, 54; C. M. Warren: Mem. Amer. Acad. (N. S.), **9**, 156.

[2] Ann. Chem. (Liebig), **144**, 10.

[3] We have since obtained 50 grams of an oil that collected at 8–9° with very small amounts above and below these limits. A vapor-density determination by the Hofmann method gave the following results:

0.0717 grams of the oil gave 45.5 cc. of vapor at 16°, and under a tension of 48.1 cm. of mercury.

Required for C_4H_{10}.	Found.
2.01	2.04

For further proof as to the composition of this distillate, an examination of its halogen and other derivatives is now in progress.

Considerable quantities of distillates collected below 30°, but by continued distillation they were mostly separated into higher and lower constituents, indicating the absence of individual products. In the vicinity of 30° the fractions were large, amounting to 300 grams between 28° and 32°. After the ninth distillation, 75 grams collected between 29° and 30°, with the barometer at 747 mm. A vapor-density determination gave 2.52; required for pentane, 2.49. This product was, therefore, isopentane, boiling-point 30°. Between 36° and 37°, 75 grams distilled, and this distillate was shown by its vapor-density to have the composition required for pentane; a vapor-density determination gave 2.49; required for pentane 2.49. This substance therefore corresponded to normal pentane, boiling-point 37° (Warren). The weights collected evidently afforded no information concerning the proportions in which these hydrocarbons are contained in the crude oil. Other results show that they are present in smaller quantities than in Pennsylvania oil.

At higher temperatures to 60°, the weights of the distillates were very small and irregular, which indicates the absence of definite compounds. Between 60° and 62°, 150 grams collected at the end of the fifteenth distillation, and this was still further reduced to 50 grams between 60° and 61°, with a vapor-density corresponding to that of hexane; found, 2.94; required for hexane, 2.98; boiling-point of isohexane, 61°.27 (Warren). After the fourteenth distillation, with the barometer at 749 mm., between 67° and 68°, 75 grams collected that distilled tolerably constant within this limit. A vapor-density determination gave 3.00; required for normal hexane, 2.98; boiling-point, 68°.5 (Warren).

For the separation of the less volatile hydrocarbons, the fraction —150°, obtained from the crude oil by distillation *in vacuo*, was subjected to further distillation under atmospheric pressure. 41.5 kilos of crude Findlay oil were distilled under a tension of 50 mm., and collected in the first distillation at —100°, 100–150°, 150–200°, 200–250°, and 250–350°. The decomposition was comparatively slight, and the fractions, especially the less volatile, were free from the disagreeable pungent odors characteristic of refinery-distillates. Even the

residue above 350° had apparently undergone very little decomposition. On account of the reduced boiling-points, it was not expected that the more volatile constituents could be collected, and it was subsequently found that scarcely any distillate boiling below 30° was condensed. The weights of the first fractions were as follows:

	—100°	100–150°	150–200°	200–250°	250–350°	Residue
Grams	8000	8520	6480	7700	2670	9000
Percentages	18.6	19.8	15.1	18.0	6.2	20.9

The specific gravity of the individual fractions was determined with the following results:

—100°	100–150°	150–200°	200–250°	250–300°	300–350°	Residue.
0.7445	0.7852	0.8161	0.8387	0.8647	0.8759	0.0130

The fraction —100° contained no hydric sulphide; the higher fractions contained it in small quantities. The percentages of sulphur in the same distillates were obtained by combustion in air:

	—100°	100–150°	150–200°	200–250°	Residue.
Sulphur	0.054	0.25	0.42	0.61	0.67

In comparing the percentages of sulphur in the vacuum-distillates with those under atmospheric pressure, it is evident that the main bodies of the sulphur compounds collect in the higher portions, leaving the fractions below 150° nearly free from sulphur.

Percentages of sulphur under atmospheric pressure:

110–150°	150–220°	220–257°	257–300°	300–350°	Residue.
0.10	0.38	0.41	0.37	0.37	0.54

It is also apparent that distillation *in vacuo* protects, to a certain extent, the sulphur compounds from decomposition. In ordinary distillation of the crude oil, as has been mentioned, sulphur is invariably observed in the condensing-tube. Even in vacuum-distillation at high temperatures decomposition cannot be wholly avoided, although the separation of sulphur has never been observed. It is probable that chemical reactions occur within the oil from the action of the various constituents upon one another, such, for example, as the action of the oxygen compounds upon the sulphur compounds. These observations furnish valuable evidence in favor of vacuum-distillation for the sulphur petroleums.

The percentage of bromine absorbed by the fractions collected *in vacuo* was also determined:

	—100°	100–150°	150–200°	200–350°	Residue.	Crude oil
Bromine	0.0	4.57	6.60	7.08	24.38	10.19

It is interesting to compare the bromine-absorption in the vacuum-distillates with the quantities absorbed in the distillates collected under atmospheric pressure:

	100–159°	150–220°	220–257°	257–300°	300–330°	+330°
Bromine	0.73	1.74	4.84	5.04	12.10	19.50

Doubtless the larger absorption of bromine in the vacuum-distillates at lower temperatures depends, at least in part, upon the fact that the sulphur compounds are protected from decomposition during distillation, and also upon the extent to which the constituents with higher boiling-points are distilled at lower temperatures under the diminished pressure. It would be expected that the residue in the distillation under atmospheric pressure should show a higher absorptive power than that collected *in vacuo*. The behavior of the higher fractions towards bromine and the nature of the decompositions by cracking will receive further attention.

The portions distilling below 150° were next submitted to prolonged fractional separations under atmospheric pressure with the aid of Hempel columns and Warren condensers. We were led to appreciate the exhaustive labors of our predecessors in their investigations on petroleum, and our indebtedness to them for the efficient means at present available for conducting such distillations. For the separation of complex mixtures, especially in considerable quantities, in point of efficiency the Warren condenser leaves nothing to be desired. It appears to effect a more rapid separation than the Hempel column, although the latter is of great service. The Hempel method has the advantage that it requires less attention, with no loss of time in heating a bath nor in maintaining a constant temperature in the bath. From the description of Warren's hot condenser given in the "Treatise on Chemistry," Vol. III, Part I, by Roscoe and Schorlemmer, an erroneous impression must have been received concerning this apparatus. On pp. 149, 150, the following words appear: An apparatus has been employed by Warren in the fractional

distillation of tar oils and petroleums. This permits a complete control over the temperature of the vapor, accomplished by an air-bath round which a spiral tube is placed, connected with the boiling-flask. The temperature of this air-bath is regulated by a lamp. The liquid used for heating the air-bath may be either water, oil, or fusible metal, and into this the thermometer is placed. . . . In distilling petroleum the difference in temperature between the boiling liquid and the air-bath was, to begin with, about 35°, or even more." The idea conveyed here is that the constant temperature is maintained by means of an air-bath, although it is evident from the following description, taken from the original memoir,[1] that there is not the remotest allusion to an air-bath: "In the new process, perfect control of the temperature of the vapors is secured by simply conducting these vapors upwards through a worm contained in a bath, the temperature of which is regulated by means of a lamp, or by a safety furnace. The bath may be of oil or water or metal for very high temperatures, as the case may require, and it is furnished with a thermometer. That this bath may be equally adapted for the separation of liquids boiling below the common temperature, an empty vessel is permanently secured in the interior of the bath by means of straps of metal across the top, to serve as a convenient receptacle for ice or ice-water, by means of which a low temperature may be steadily maintained. This interior vessel also serves a good purpose in economizing time and fuel in heating the bath, and it diminishes the quantity of oil required to cover the worm. It is made to extend to within about three inches of the bottom of the bath, and large enough to fill a greater part of the space in the center of the coil." It will therefore be seen that it was not Warren's intention to use this apparatus in any sense as an air-bath. It is to be used solely as a liquid-bath.

Since the principal object was to identify the individual constituents and to determine their approximate quantities, it was only necessary to collect our products within such close limits of temperature comparable with boiling-points already accurately determined that they should yield satisfactory

[1] Mem. Amer. Acad. (N. S.), 9, 125.

analytical data. In successive distillations, collecting at first within 5°, then within 2°, and finally within 1°, after the first distillation the fractions collected rapidly, with increasing quantities at temperatures near boiling-points of well-known hydrocarbons C_nH_{2n+2}, and at certain other points at which an equilibrium in boiling-points seemed to be established by mixtures. It was only with much difficulty that some of these mixtures could be separated into their constituents. We had occasion to recall the remark of Warren concerning the greater amount of labor involved in determining the absence of definite compounds in such mixtures than in proving the presence of well defined hydrocarbons. The fractions containing the aromatic hydrocarbons will be considered together. The products collected for vapor-density determinations were purified as completely as possible by the removal of unsaturated hydrocarbons, sulphur compounds, and the aromatic hydrocarbons. For the removal of sulphur compounds, each fraction was thoroughly agitated with alcoholic mercuric chloride. After washing with water there remained in solution not more than 0.02 or 0.03 per cent. of sulphur when the mercuric chloride gave a crystalline precipitate, which was the case in distillates below 150°, provided they were collected at first *in vacuo*. In a former paper[1] it was stated that alcoholic mercuric chloride removed two-thirds of the sulphur. Those experiments were made with refinery distillates, which do not behave the same towards mercuric chloride as vacuum-distillates. In higher fractions somewhat more sulphur is retained, and with increasing boiling-points even the mercury itself in considerable quantity may be held in clear solution, either in the form of $HgCl_2R_2S$, or in some other combination. This peculiarity has occasioned us much trouble in purifying distillates above 200°. In some of these products, hydric sulphide in the cold will not precipitate the mercury; frequently it is only after prolonged action with the aid of heat that the mercury can be completely removed. These sulphur oils seem to possess the property of dissolving metals, metallic oxides, and other compounds, which has been observed in other petroleums. The action of paraffin

[1] This JOURNAL, 16, 88.

oils on metals has been examined by Macadam,[1] who finds that lead, solder, and zinc are quite readily, tin and iron but slightly, affected. Some oils have a greater solvent action than others, and Macadam attributes it to the hydrocarbons. Engler[2] repeated the experiments of Macadam, and observed that metals were not affected when air is excluded. It was therefore inferred that acid compounds are formed in the oil by exposure to air, and also metallic oxides, which are dissolved by the acids. Engler does not attribute the solvent action to ozone. It is probable that the purification of refinery-distillates from the sulphur petroleums, by agitation with an alkaline solution of plumbic oxide, depends, at least in part, upon the solvent action of certain constituents of the oil. Oxygen compounds, which are doubtless present in these oils, may assist the action, as has been observed in other oils. This subject will receive further attention when we reach the higher distillates.

After removal of the sulphur compounds, each distillate for vapor-density determination was thoroughly agitated, first with concentrated nitric, then with concentrated sulphuric acid, washed, and dried. Finally, under a return condenser, it was heated for some time with metallic sodium.

From 41.5 kilos, distilled *in vacuo*, at the end of the eighth distillation, the last seven under atmospheric pressure, the following weights were obtained with much smaller quantities outside these limits:

	−55°	58–62°.	65–68°.	77–83°.
Grams	15	120	310	85

As already mentioned, on account of loss from the diminished pressure, as well as the unavoidable loss in any distillation, the weights of the lower fractions collected *in vacuo* evidently cannot be accepted as representing even approximately the quantities present in the crude oil.

Between 87° and 93°, 80 grams collected after the sixth distillation, and in the portion which distilled constant at 89–90°, bar. 754 mm., a vapor-density determination gave 3.43; required for isoheptane, 3.46; boiling-point 90°.4 (Warren).

At the end of the sixth distillation, 175 grams collected at

[1] J. Chem. Soc., 1878, p. 355. [2] Ber. d. chem. Ges., 11, 2186.

96–99°, and 50 grams distilled constant at 86–97°, bar. 744 mm.; a vapor-density determination of this product gave 3.42; required for heptane, 3.6; boiling-point of heptane, 98.°7 (Warren). Above this point the distillates were small in amount to 109°, where other products began to appear; between this point and 120° the single degree fractions were considerable in quantity.

At 118–120°, 120 grams were collected, of which 50 grams distilled constant at 119–120°, bar. 749 mm. This product gave a value in a determination of its vapor-density required for octane: found, 3.98; required, 3.94. Since some doubt has been expressed concerning the existence of an octane with this boiling-point, this fraction was carefully purified for analysis, with alcoholic mercuric chloride, nitric acid, and sulphuric acid, and it was finally submitted to prolonged boiling with sodium. Determinations of carbon and hydrogen then gave the following results:

I. 0.1707 gram oil gave 0.5282 gram CO_2 and 0.1707 gram H_2O.

II. 0.2017 gram oil gave 0.6237 gram CO_2 and 0.2737 gram H_2O.

	Calculated for C_8H_{18}.	Found. I.	II.
C	84.20	84.42	84.28
H	15.79	15.19	15.08

The low percentage of hydrogen evidently indicated that the octane was still contaminated by a hydrocarbon containing less hydrogen. For further purification the oil was heated to boiling during several hours with a mixture of nitric and sulphuric acids, and boiled several times with sodium. It then gave the percentages of carbon and hydrogen required for octane:

	Required for C_8H_{18}.	Found.
C	84.20	84.20
H	15.79	16.10

There seems to be no question that the fraction 118–119° contains a hydrocarbon with the composition required for octane, and this observation is apparently confirmed by the results of others. Warren[1] separated a constituent of Pennsyl-

[1] Proc. Am. Acad., 27, 78.

vania petroleum distilling constant at 119°.5 (cor.), which gave a vapor-density corresponding to that of octane. From the extraordinary care with which the determinations of Warren were made, there can be no doubt as to the existence of a hydrocarbon with this boiling-point in Pennsylvania petroleum. Although hexahydroisoxylol has been recognized by Beilstein and Kurbatoff,[1] it is probably not the principal constituent with this boiling-point of the Pennsylvania oil; it is certainly not of the Ohio oil.

From coal-oil, Schorlemmer[2] separated an octane boiling at 119–120°, and subsequently he identified the same body in petroleum boiling at 119°. The following data are taken from his original publication:

	Required for C_8H_{18}.	Found.
C	84.20	84.10
H	15.79	16.10
Vapor-density	3.98	3.95

In the "Treatise on Chemistry," by Roscoe and Schorlemmer, (New York, 1886), it is stated that the three octanes known are normal octane, boiling-point 125°.46, found in petroleum; tetramethylbutane, boiling at 108°.5; and hexamethylethane, melting at 96–97° and boiling at 105–106°. This enumeration does not recognize an octane boiling at 119° in petroleum. It would seem that our fraction from the Ohio oil was prepared with sufficient care to preclude the possibility of a mixture of higher or lower constituents. We shall endeavor to obtain independent evidence as to the identity of this fraction by a study of its chemical reactions, and the preparation of its derivatives.

The following suggestions, which I have taken from one of the private papers, dated 1868, of Mr. Warren, through the kindness of Professor Storer, indicates that Warren recognized the possibility of a series containing less hydrogen: "The samples analyzed may have contained traces of more highly carbonized substances, and that it would be worth while to treat with $HOSO_3$ and $HONO_2$, and remove these." Beilstein and Kurbatoff met with the same difficulty in the fraction 95–100° and 118–120° in their attempts to ascertain the

[2] Ber. d. chem. Ges., 13, 2028. [1] J. Chem. Soc., 15, 419.

presence in the Pennsylvania oil of the hexahydro series. The series with less hydrogen seems to be removed only very slowly even by vigorous treatment with a mixture of nitric and sulphuric acids.

In continuing the separations above 120°, after the eleventh distillation the oils collected in considerable quantities within the limits of one degree :

	120–121°	121–122°	122–123°	123–124°	124–125°	125–126°	126–127°	127–128°
Grams	35	40	80	70	75	75	60	40

Notwithstanding our endeavors to separate the fractions 122–125° into higher and lower constituents, they may still be mixtures; aromatic derivatives are here present in small quantity. If in more prolonged separations distillates still persist within the same limits, they will be submitted to careful study in their behavior toward chemical reagents.

The greater portion of the fraction 125–130° was unfortunately lost by an accident after the eleventh distillation. Sufficient however was collected at 127–128° for a vapor-density determination; it gave, by the method of Dumas, the value required for the formula C_9H_{18}; found 3.90, required 3.94. To the liquid collected by Warren at this point was assigned the boiling-point 127°.6; the vapor-density found by him was 3.99, and those observations seem to be confirmed by our results with the Ohio product. The portions distilling between 115° and 130° evidently need to be carefully examined in larger quantities with particular reference to the octanes. The distillates collected between 130° and 145° will be considered in connection with the aromatic compounds.

Between 144° and 148°, after many distillations, the fractions were small in quantity. At the end of the sixth distillation, 65 grams collected at 149–151°, of which 40 grams distilled constant at 149–150°, barometer 756 mm. After prolonged heating with concentrated nitric acid a nitro compound was formed that remained chiefly in solution in the oil. Upon dilution of the acid an oily liquid separated in small quantities. But when the oil was shaken with sodic hydrate, it became intensely red in color, and by repeated washing with the alkaline solution the nitro product was in part removed, and it separated again as an oil by acidifying the solution. After

washing, the remaining oil was dried and heated to boiling during several hours with sodium. It was then distilled from the large quantity of solid that had separated, and the greenish yellow distillate again boiled with sodium. Still more solid separated, and after distillation the oil was again treated with sodium until there was no further action. The boiling-point was not appreciably changed by this treatment, although it was evident that some constituent had been removed capable of forming a nitro derivative soluble in alkalies. The residual oil was shown by vapor-density determinations and analysis to have the composition required for nonane. The boiling-point of nonane is 150°.8 (Warren).

I. 0.1799 gram oil gave 0.3987 gram CO_2, and 0.1749 gram H_2O.

II. 0.1751 gram oil gave 0.5424 gram CO_2, and 0.2488 gram H_2O.

	Calculated for C_9H_{20}.	Found. I.	Found. II.
C	84.37	84.96	84.48
H	15.63	15.16	15.88

Analysis I. was made of the oil after treatment with alcoholic mercuric chloride, but before heating with the acid mixture; analysis II. of the oil after treating with a mixture of nitric and sulphuric acids and boiling with sodium.

The determinations of vapor-density of this product in the appparatus of Victor Meyer, with a bath of ethyl benzoate, gave the following results: I. 4.73; II. 4.74; required for C_9H_{20}, 4.43.

This fraction therefore contains nonane, although it consists to a very considerable extent of another hydrocarbon, which seems, by the ready formation of nitro compounds and its behavior toward alkaline solvents, to be a member of the series C_nH_{2n}. All the fractions of the Ohio oil that we have examined below 150° are similarly contaminated by, or rather contain in appreciable quantities, hydrocarbons which form nitro products with the characteristic qualities of an unsaturated or paraffin nitro compounds.

Thus far Ohio petroleum has proved to contain members of the series C_nH_{2n+2}, corresponding to those which have been

identified in Pennsylvania oil, but in much smaller quantities. They form one-fifth of the crude Pennsylvania oil and less than one-tenth of Ohio oil.

In identifying these constituents it has not seemed necessary to accumulate data further than would appear essential in showing the similarity of our products to those whose composition has been so carefully demonstrated in Pennsylvania petroleum. And while this portion of our labor may be of less interest than the study of the constituents with higher boiling-points, it has seemed of sufficient importance to justify the necessary expenditure of time and effort. The higher fractions have been quite thoroughly distilled entirely *in vacuo* to avoid decomposition so far as possible, and these products, as well as the residue above 350° of the first vacuum-distillate, are reserved for later study.

(To be continued.)

ON THE COMBINATION OF ANHYDROUS AMMONIA AND ALUMINIUM CHLORIDE.

By J. M. Stillman and Minnie B. Yoder.

The compounds resulting from the action of dry ammonia upon anhydrous metallic salts, especially the halogen salts, have been more or less carefully studied by chemists, notably by H. Rose and by Rammelsberg, though many others have contributed to the interesting data. Inspection of the results of these investigations shows that no very satisfactory relation can be perceived between the composition of these compounds and the natural-group relationships of the elements from which they are derived. It appeared to be of interest to study some of these compounds more carefully to see if such relationship might not be found to exist, and if, from this as a starting point, some clue might not be obtained to the chemical nature of such compounds. The replaceability of water by ammonia in hydrated copper sulphate noted by Mendelejeff[1] lends additional interest to the study of these compounds. Like the combined water in salts the ammonia in these addition-products furnishes a good illustration of a kind of chemical union, but little understood and frequently characterized

[1] Ber. d. chem. Ges., 3, 422.

as "Molecular Combination." As conflicting data exist concerning the composition of the combinations of ammonia and ferric chloride, the action of ammonia upon ferric and ferrous chlorides was first studied, the investigation being carried on by Mr. A. S. Miller.[1] The result of this investigation was to show that ferric chloride combines with dry ammonia to form $FeCl_3.6NH_3$, a light, reddish, non-deliquescent powder, which loses ammonia to the air, leaving $FeCl_3.5NH_3$ as a compound relatively more stable in dry air. At higher temperatures it loses ammonia with gradual oxidation and formation of ammonium chloride. The action of ammonia upon ferrous chloride was found to conform to earlier data, yielding a white powder $FeCl_2.6NH_3$, losing $4NH_3$ at 100° in dry hydrogen.

The general similarity of aluminium and ferric compounds suggested that the ammonia compounds of aluminium chloride be next studied.

The data on this subject are comprised in the investigations of Persoz[2] and H. Rose.[3] The former obtained a compound containing as high as 27.6 per cent. ammonia; the latter one containing 25.7 per cent., thus suggesting $AlCl_3.3NH_3$ (or $Al_2Cl_6.6NH_3$) as the formula (theory, 27.7 per cent). The re-investigation of this combination was taken up much on the same lines as were laid down for the study of the iron compounds. The aluminium chloride was obtained by heating aluminium foil in a current of carefully dried chlorine gas. The chloride was purified by sublimation in the same tube and current of chlorine in which it was prepared. It possessed a yellow color and gave a faint test for iron, but was practically pure.

Al found	20.46
Al in $AlCl_3$ (calculated)	20.52

The treatment with ammonia gas was at times undertaken in a U bent in the cumbustion-tube, in which the chloride was prepared, or else the chloride was transferred with especial care to avoid access of atmospheric moisture to an ordinary U-tube. To avoid so far as possible secondary reactions resulting from the heat of reaction on absorption of ammonia,

[1] This JOURNAL, **17**, 570.
[2] Ann. chim. phy. [?], **44**, 320; cited by Graham-Otto, 5th Auf. IV, **2**, 31.
[3] Cited by Graham-Otto: *loc. cit.*

the U-tube was immersed in water and carefully dried ammonia was passed through, at first very slowly and mixed with much air. Only when the granular yellowish chloride had fallen into a fine white powder was ammonia passed through so as to replace the air in the apparatus to effect complete saturation. The entire time thus employed for saturation was usually about twenty hours. The resulting product is a white and very light powder, occupying many times the volume of the original chloride.

It is not deliquescent, and when thrown into water is not dissolved, but passes over naturally into hydrate of aluminium. It smells strongly of ammonia.

The following analyses were made each from an independent preparation:

	I.	II.	III.	IV.		Calculated for $AlCl_3.6NH_3$.
Al	11.47	11.49	11.47	11.66		11.47
Cl	44.53	44.64	44.73	44.89		45.22
NH_3	39.92	40.96	41.51	41.40	41.94	43.31
	95.92	97.09	97.71	97.95	98.49	100.00

It will be seen that the ammonia falls noticeably short and that the total percentages are short of 100. We shall have occasion to speak of this later, but in general it will be seen that the analyses point unmistakably to the formula $AlCl_3.6NH_3$ as expressing the composition of the saturated product.

In view of the results of Persoz and of Rose above quoted, attempts were made to ascertain the stability of this compound at various temperatures in perfectly dry air, by passing a slow current of dried air through U-tubes containing the saturated product.[1] The U-tube was reimmersed in a water or paraffin-bath and the temperature regulated as desired. The results obtained were not what we had anticipated. While the determination of aluminium and chlorine in samples treated at tem-

[1] Great care was taken to dry all the gases thoroughly; chlorine was passed through concentrated sulphuric acid and glacial phosphoric acid; ammonia was generated by dropping ammonia-water on stick potash, and dried through two cylinders of stick potash and two of quick-lime; air was passed through sulphuric acid and through cylinders of stick potash and phosphoric acid. Appropriate drying tubes were also connected beyond the U-tubes to prevent the entrance of moisture from that direction.

peratures from 20° to 120° were approximately such as to indicate a composition $AlCl_3.5NH_3$, the ammonia determinations fell considerably short of the percentage theoretically present.

The following examples will illustrate:

Time treated by current of dry air.	Temperature.	Per cent. Al.	Per cent. Cl.	NH_3.
48 hours	20–25°	11.69	45.25	31.77
72 "	20–25°	12.57	48.19	33.03
9 "	100°			
24 "	100°	12.37	47.03	23.23
120 "	20–25°	12.07	48.04	undet.
5 "	100°			
4 "	120°	12.21	49.01	?
100 "	20–25°	12.23	46.82	21.80
13 "	110°			
Calculated for $AlCl_3.5NH_3$		12.36	48.74	38.90

When we first met with these results we feared that the loss of ammonia had been more or less compensated by absorption of moisture, but increased precautions to obviate this contingency made this explanation improbable. We were then forced to conclude that a more radical decomposition takes place. We also noticed that in two instances drops of moisture collected on the cooler parts of the tube when the current of air had been interrupted for a time, and the temperature of the U-tube was above 100°. We could not account for this except on the assumption that the water was produced by the oxidation of the hydrogen of the ammonia.

To test this tendency to oxidation, dry air was passed over a portion of the saturated ammonia compound heated to about 200° for a period aggregating twenty-four hours. A noticeable deposition of moisture took place when the air current was interrupted. Ammonium chloride was produced and collected by volatilization in the cooler parts of the tube as a well characterized crystalline sublimate.

The analysis of the substance remaining in the U-tube gave

Al	28.10
Cl	31.11
NH_3	15.87
	75.08

If we here assume that all the aluminium has been oxidized

to the oxide Al_2O_3, and that all the chlorine is present as ammonium chloride—ignoring for the moment the determination of ammonia above given—we should have for 28.10 per cent. aluminium, 24.96 per cent. oxygen, and for 31.11 per cent. chlorine we should have 15.82 per. cent. ammonium. The 15.87 per cent, ammonia above found would correspond to 16.81 per cent. ammonium. The analyses would then be expressed:

Al	28.10
O	24.96
Cl	31.11
NH_4	15.82
	99.99

These results taken in connection with the observed formation of water and the isolation of some ammonium chloride by sublimation render the result of the oxidation process quite plain.

We also are disposed to connect the shortage in ammonia and in totals of analyses in the original preparation with this oxidation. In spite of the cooling of the U-tubes during absorption, it is probable that the very considerable energy of the chemical action produces local increase of temperature and consequent oxidation of the aluminium and of the ammonia. If instead of using air to dilute the ammonia we had used nitrogen or hydrogen, it is probable that results still more close to the theory would have been obtained.

A couple of experiments were made to determine the stability of the preparations at higher temperatures in a current of hydrogen.

A portion of the saturated compound (analyzed under III) was heated for ten hours at 200–240° in a current of dry hydrogen. The semi-fused and somewhat hygroscopic mass gave the following results on analysis:

		Calculated for $AlCl_3.2NH_3$.
Al	16.12	16.1
Cl[1]	59.45	63.6
NH_3	19.76	20.3
	95.33	100.00

[1] Not enough of the preparation remained to duplicate this analysis as seemed desirable.

A portion of the saturated compound (analysis under IV.) was submittted to a current of dry hydrogen for twelve hours at room-temperature to replace air thoroughly and then heated in a free current of hydrogen for six hours at 100°.

The analysis gave :

		Calculated for $AlCl_3.5NH_3$.
Al	12.03	12.36
Cl	47.56	48.74
NH_3	35.03	38.90
	94.62	100.00

As the original preparations were slightly oxidized, no very satisfactory analyses were to be expected from these preparations. While the hydrogen was thoroughly dried it was not purified from possible contamination with other impurities. Nor is any stress placed here upon the definiteness of these compounds, nor their stability at the temperatures given, but a general idea of the stability of the combination at various temperatures may be obtained from the above results.

It did not seem advisable at present to repeat the investigation out of contact with oxygen for the sake of obtaining more exact analyses. It is intended to pursue in this laboratory the investigation of the action of dry ammonia upon other anhydrous chlorides, and it is not improbable that side-lights will be shed upon some of the questions raised in the foregoing from the behavior of other compounds.

Special emphasis is here laid upon the evident similarity of the results of the action of ammonia upon the chlorides of iron and aluminium.

LELAND STANFORD, JR. UNIVERSITY, August, 1895.

THE CHEMICAL KINETICS OF OXIDATION.

By Herman Schlundt and Robert B. Warder.

I.—ON THE SPEED OF THE LIBERATION OF IODINE IN MIXED SOLUTIONS OF POTASSIUM CHLORATE, POTASSIUM IODIDE, AND HYDROCHLORIC ACID.[1]

By Herman Schlundt.

A systematic study of the conditions of experimentation that determine the progress of a reaction has until of late years received very little attention. During the last two decades the speed of various reactions as dependent upon modifying influences has been specially investigated, and to-day the subject of chemical dynamics furnishes many interesting problems for investigation. The present work has been undertaken with the view of collecting data for the solving of some of these problems.

Burchard[2] studied the speed of the liberation of iodine in mixtures of hydriodic and iodic acids in very dilute solutions. Similarly he investigated mixtures of hydriodic acid with bromic or chloric acids. Mixtures of the salts of hydriodic and chloric acids with hydrochloric acid, however, have never to my knowledge been investigated in this way. It is the purpose of this paper to study the speed of the liberation of iodine in such mixtures as are influenced: first, by temperature; second, by degree of concentration; third, by the presence of an excess of one or more of the components; and fourth, by the addition of an excess of other acids.

Preliminary Experiments.—It is well known that when potassium iodide, potassium chlorate, and hydrochloric acid are mixed in solution, iodine is liberated according to this reaction.

$$KClO_3 + 6HCl + 6KI = 6KCl + 3H_2O + I_6.$$

In order to ascertain the conditions favorable for studying the speed of the liberation of iodine in such mixtures, several preliminary experiments on the effects of temperature and concentration became necessary. It was found that in mix-

[1] This paper is an abstract of a thesis submitted for the degree of Bachelor of Science in the General Science Course, University of Wisconsin, June, 1894, and issued as a Bulletin of the University in the same year.

[2] Ztschr. phys. Chem., 2, 796, (1888).

tures containing equivalents[1] of the salts according to the foregoing reaction as decinormal solutions at 0° iodine is liberated very slowly, a sample of 20 cc. of the mixture after twenty-four hours requiring only 0.1 cc. of a decinormal solution of sodium thiosulphate to destroy the blue color produced by the addition of starch-paste. The same mixture at 100° proved well adapted for investigation, as the following table shows:

Duration of reaction in minutes.	Cc. of solution taken.	Cc. of n-20 $Na_2S_2O_3$ used in each titration.	Per centage of iodine liberated.
15	20	1.45	3.6
35	20	3.1	7.8
60	20	4.3	10.8
90	20	6.0	15.0

Preparation of Solutions.—The solutions used were prepared as follows: A normal solution of potassium iodide free from iodate served throughout the investigation. It was prepared by dissolving 165.54 grams of the pulverized salt, dried at 100°, and making it up to one liter. The normal hydrochloric acid was standardized on calcite. The potassium chlorate was tested for sulphates, nitrates, chlorides, the heavy metals, and the alkaline earths, and found to be pure. The solution of this salt was three times normal and was prepared by taking 61.25 grams of the dry crystallized salt to a liter. A twentieth-normal solution of sodium thiosulphate served for titration. It was prepared by dissolving 12.4 grams of the pure crystallized salt per liter of water. The strength of this solution was verified by testing with decinormal iodine solution. The starch-paste used was quite dilute and was prepared by stirring up 2-3 grams of the fine starch with cold water; 300–400 cc. of boiling hot water were then added and the mixture well stirred. This paste was then filtered, and the filtrate used as indicator. A fresh solution was frequently prepared.

Conduct of Experiments.—The entire series of investigations was conducted at 100°. The mixtures were prepared by measuring out the desired equivalents of the different components, cooling them to 0° in ice-water, and then mixing

[1] Whenever this term is used it is understood to mean equivalents according to the reaction already given.

them. Samples of 20 cc. of the mixture were then quickly taken out and put into ordinary six-inch test-tubes. The tubes were quickly sealed, but all the time kept as cool as possible. The samples were then plunged into a large kettle of boiling water and kept at this temperature. At definite intervals samples were taken out and plunged into ice-water, thus quickly checking the reaction. After one minute the test-tubes were broken, washed with cold water, and the iodine determined by means of a twentieth-normal solution of sodium thiosulphate.

The test-tubes were sealed at about the same distance from the end, thus keeping the pressure nearly constant. Whenever it was found expedient to work with samples of 10 cc. the tubes were used over again. As the test-tubes were new, special precautions in cleaning had to be exercised. To remove the alkalies that are given off by new glassware, I followed the advice of Professor Ostwald and steamed the tubes for about five minutes by means of an apparatus figured on p. 295 of his "Hand- und Hilfsbuch zur Ausführung physico-chemischer Messungen."

In mixtures where the components enter in equivalent proportions it was found that the free iodine began to crystallize out when about 40 per cent. had been liberated. To get this iodine into solution a few cc. of a strong potassium iodide solution were added. But as this excess of potassium iodide might possibly enter into the reaction and so slightly increase the amount of sodium thiosulphate used, the iodine of several samples was shaken out with carbon bisulphide and determined. A comparison of results obtained by these two methods,[1] shows that the addition of a few cc. of cold potassium iodide during titration has little or no effect on the result.

The equation expressing the reaction shows that for every molecule of potassium iodide present one atom of iodine is liberated. In titrating the iodine with sodium thiosulphate the following reaction takes place :

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

Hence the per cent. of iodine liberated at any time from the given sample (originally containing 20 cc. of potassium

[1] Sec. B, III, series (1) and (3), and Sec. C, series (4).

iodide in decinormal solution) is obtained by dividing by 40 the number of cc. of sodium thiosulphate used, the thiosulphate being twentieth-normal.

Presentation of Results.—The results obtained are divided into 5 sections. Section A includes the results obtained from a mixture containing equivalents of the salts as decinormal solutions. The effect of a definite excess of *one* of the several components upon the speed of the reaction is shown in Section B. Section C, similar to B, gives the effect upon the speed when definite excesses of *both* potassium iodide and hydrochloric acid are used. Section D gives the results obtained from mixtures containing equivalents of the components in fifth-normal and two-fifths-normal solutions respectively. The acceleration in the speed by various organic and inorganic acids forms the fifth and last section of the results.

To facilitate comparison, the results obtained in similar series are graphically represented in the same figure. In plotting the curves the axis of abscissas was chosen to denote the time of the reaction, each space representing one hundred minutes, while the percentages of iodine liberated are plotted on the axis of ordinates.

The results are given in condensed form in the following tables.

Table I shows the progress of the reaction:

A, with equivalent decinormal amounts, according to the reaction: $KClO_3 + 6HCl + 6KI = 7KCl + 3H_2O + I_6$; B, with two-fold quantity of chlorate at the beginning; C, with three-fold quantity; and D, with four-fold quantity of chlorate at the beginning.

A sample of 400 cc. of the mixture A was prepared as follows:

Normal hydrochloric acid	40.0 cc.
Normal potassium iodide	40.0
Three-times normal potassium chlorate	13.3
Water	306.7
	400.0

20 cc. of the mixed solution were taken for each titration:

TABLE I.

Time in minutes.	Cc. n-20 $Na_2S_2O_3$ used in each titration.[1]				Percentage of iodine liberated.			
	A.	B.	C.	D.	A.	B.	C.	D.
10		1.35		2.8		3.4		7.0
15	1.45		2.8	5.0	3.6		7.0	
20		2.85				7.1		12.5
30		3.95 3.9	5.0	5.0		9.9 9.8	12.5	
35	3.1 3.0				7.8 7.5			
40				8.25				20.6
55			8.0				20.0	
60	4.3	6.6 6.7		10.6	10.8	16.5 16.8		26.5
70	4.6				11.5			
85			10.95	13.5			27.4	33.8
90	6.0				15.0			
100		9.9				24.8		
110	6.6			15.4	16.5			38.5
120			12.7				31.8	
150	7.85		14.25	17.35	19.6	35.6		43.4
170		13.0				32.5		
180				19.25				48.1
210	9.4		16.65	20.25	23.5		41.6	50.6
230				21.4				53.5
270		16.9				42.3		
290				21.85				54.6
300	12.05 12.25				30.1 30.6			
360	13.55				33.9			
400			21.45				53.6	
420		18.95				47.4		
440	14.55			24.2	36.4			60.5
510				24.75				61.9
520	15.55				38.9			
585	16.0				40.0			
590		21.2	23.9	25.6		53.0	59.8	64.0
730	17.0				42.5			
830	18.4			27.4	46.0			68.5
900				27.8				69.5
1250	21.3				53.3			
1320		28.85	28.95	31.3		64.6	72.4	78.3
1400	22.7				54.3			
1830	23.2				58.0			
2000	24.1				60.3			

[1] See curves A, B, C, and D in Figure 1.

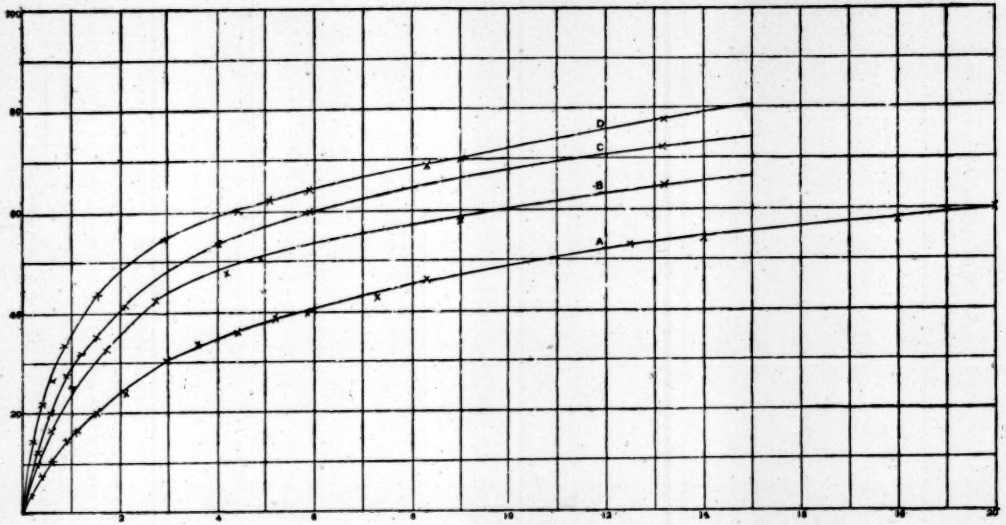

D
C
B
A
2
4
6
8
10
12
14
16
18
20

Table II shows the progress of the reaction:

A, with equivalent decinormal solutions; B, with two-fold quantity of potassium iodide, at the beginning; C, with three-fold quantity; and D, with four-fold quantity.

TABLE II.

Time in minutes.	Cc. n-20 $N_2S_2O_3$ used in each titration.[1]				Percentage of iodine liberated.			
	A.	B.	C.	D.	A.	B.	C.	D.
10			1.8	1.9			4.5	4.8
15	1.45	2.4			3.6	6.0		
20			3.25				8.1	
25				4.6				11.5
30		4.7				11.8		
35	3.1 3.0				7.8 7.5			
40			5.9	6.7			14.8	16.8
50		6.35				15.9		
60	4.3			9.5	10.8			23.8
65			8.25				20.6	
70	4.6				11.5			
85		9.65		11.5		24.1		28.8
90	6.0				15.0			
100			11.05				27.6	
110	6.6	11.45			16.5	28.6		
115				13.75				34.4
150	7.85		14.6	17.1	19.6		36.5	42.8
160		13.85				34.6		
175				17.4				43.5
210	9.4				23.5			45.8
215				18.3				
225			17.8				44.5	
230		16.7				41.8		
275				21.15				52.9
300	12.05 12.25				30.1 30.6			
315		18.55				46.4		
340				22.6				56.5
360	13.55				33.9			
370			21.7				54.3	
430		19.9				49.8		
440	14.55				36.4			
450				24.2				60.5
470			24.0				60.0	
520	15.55				38.9			
530		21.4				53.5		
585	16.0		25.35		40.0		63.4	

[1] See corresponding curves, Fig. II.

A
B
C
D

Time in minutes.	Cc. n-20 $Na_2S_2O_3$ used in each titration.[1] A.	B.	C.	D.	Percentage of iodine liberated. A.	B.	C.	D.
600				26.3				65.8
640		22.9				57.3		
720			26.65	28.0			66.6	70.0
730	17.0				42.5			
760		23.65				59.1		
830	18.4				46.0			
1250	21.3				53.3			
1320				31.0				77.5
1360		27.2				68.0		
1400	21.7				54.3			
1830	23.2				58.0			
2000	24.1				60.3			

Table III shows the progress of the reaction:

A, with equivalent decinormal amounts; B, with two-fold quantity; C, with three-fold quantity; D, with four-fold quantity of hydrochloric acid at the beginning.

TABLE III.

Time in minutes.	Cc. n-20 $Na_2S_2O_3$ used in each titration.[2] A.	B.	C.	D.	Percentage of iodine liberated. A.	B.	C.	D.
10			4.6				11.5	
15	1.45				3.6			
17		4.3				10.8		
20			9.05	15.3			22.6	38.3
30		7.25				18.1		
35	3.1				7.8			
	3.0				7.5			
40			14.75				36.9	
50		10.45		24.55		26.1		61.4
60	4.3		18.75		10.8		46.4	
70	4.6	12.7			11.5	31.8		
90	6.0				15.0			
100			23.6	31.7[3]			59.0	79.3
				81.8				79.5
105		16.35[3]				40.0		
		16.2				40.5		
110	6.6				16.5			
130			25.35				63.4	
150	7.85	18.95			19.6	47.4		
200				37.15				92.9
210	9.4		30.1		23.5		75.3	
220		22.3				57.5		
295			34.95				87.4	

[1] See corresponding curves, Fig. II.

[2] See corresponding curves, Fig. III.

[3] Iodine shaken out with carbon bisulphide.

III

Time in minutes.	Cc. n-20 $Na_2S_2O_3$ used in each titration.[1]				Percentage of iodine liberated.			
	A.	B.	C.	D.	A.	B.	C.	D.
300	12.05 12.25	24.85		38.85	30.1 30.6	62.1		97.1
360	13.55				33.9			
440	14.55				36.4			
450		27.55				68.9		
460				39.55				98.9
520	15.55				38.9			
525			37.5				93.8	
585	16.0				40.0			
720		30.95				77.4		
730	17.0				42.5			
830	18.4				46.0			
1250	21.3				53.3			
1400	21.7				54.3			
1830	23.2				58.0			
2000	24.1				60.3			

[1] See corresponding curves, Fig. III.

IV.

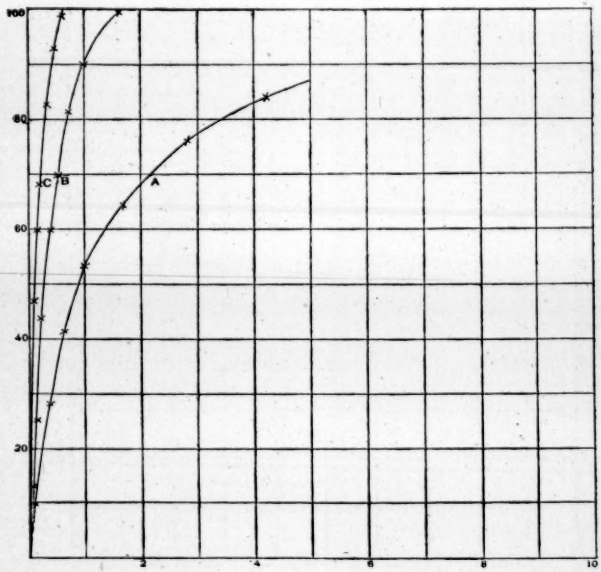


Table IV shows the progress of the reaction:

A, with two-fold quantities; B, with three-fold quantities; C, with three-fold quantities of hydrochloric acid and potassium iodide at the beginning; D, with two-fold quantity of potassium iodide and six-fold quantity of hydrochloric acid at the beginning.

In series B, C, and D 10 cc. of the mixed solution were taken for each titration.

TABLE IV.

Time in minutes.	Cc. n-20 $Na_2S_2O_3$ used in each titration.[1]				Percentage of iodine liberated.			
	A.	B.	C.	D.	A.	B.	C.	D.
5		2.6	5.4	7.3[2]		13.0	27.0	36.5
10	3.75	5.05	9.4	11.6	9.4	25.3	47.0	58.0
15			12.0				60.0	
20		8.75	13.7	15.4[2] / 15.45		43.8	68.5	77.0 / 77.3
25			25.3				76.5	
30			16.5				82.5	
31				17.65				
35	11.35	12.0	17.3	18.1[2]	28.4	60.0	86.5	88.5
45			18.6	19.0			93.0	90.5
50		14.15				70.8		95.0
55			19.75				98.8	
60	16.5		19.95	19.9[2]	41.3		99.8	
70		16.25				81.3		99.5
80			19.9				99.5	
85				19.9				
95		17.85				89.3		99.5
100	21.3				53.3			
105			20.1				100.5	
160		19.8				99.0		
170	25.75				64.4			
280	30.4				76.0			
415	33.6				84.0			

Table V shows the progress of the reaction:

A, with equivalent decinormal amounts; B, with equivalent fifth-normal amounts; C, with equivalent two-fifths normal amounts.

In series B and C 10 cc. of the mixed solution were taken for each titration; in series A, 20 cc. were taken for each test.

[1] See corresponding curves, Fig. IV.

[2] Iodine shaken out with carbon bisulphide.

A
C
B
4
100
80
60
40
20
0
2
4
6
8
10
12

TABLE V.

Time in minutes.	Cc. n-20 $Na_2S_2O_3$ used in each titration.[1]			Percentage of iodine liberated.		
	A.	B.	C.	A.	B.	C.
10		4.45	24.25		11.1	30.3
15	1.45			3.6		
20		6.7	33.7		16.8	42.1
30			38.4			48.0
35	3.1 3.0			7.8 7.5		
50		11.95	43.3		29.9	54.1
60	4.3			10.8		
70	4.6			11.5		
90	6.0			15.0		
100			50.55			63.2
110	6.6			16.5		
115		17.3			43.3	
150	7.85			17.35		
180			55.6			69.5
190		20.1			50.3	
210	9.4			23.5		
280			58.7			73.4
300	12.05 12.25			30.1 30.6		
310		22.5			56.3	
360	13.55			33.9		
410		23.9	61.75		59.8	77.2
440	14.55			36.4		
520	15.55			38.9		
530		25.15			62.9	
585	16.0			40.0		
660			65.0			81.25
750	17.0			42.5		
780		26.65			66.6	
830	18.4			46.0		
1250	21.3			53.3		
1380		29.2			73.0	
1400	21.7			54.3		
1830	23.2			58.0		
1980		30.4			76.0	
2000	24.1			60.3		

Table VI shows the progress of the reaction in fifth-normal solutions:

A, with no excess of acid at the beginning; B, C, D, and E, with a definite excess of sulphuric acid, nitric acid, hydro-

[1] See corresponding curves, Fig. V.

chloric acid, and hydrobromic acid, respectively, at the beginning.

The following is a general sample mixture of 200 cc. :

Normal hydrochloric acid	40.0 cc.
Normal potassium iodide	40.0
Three-times normal potassium chlorate	13.3
Normal acid used as accelerator	20.0
Water	86.7
	200.0

10 cc. of the mixed solution were taken for each titration.

TABLE VI.

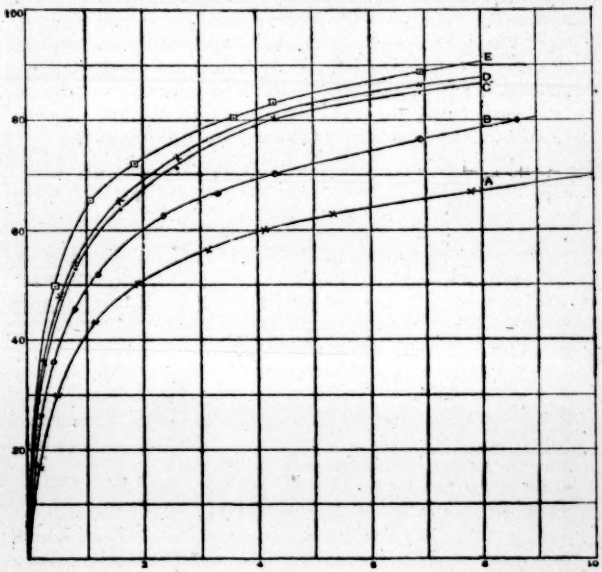
Time in minutes.	Cc. n-20 $Na_2S_2O_3$ used in each titration.					Percentage of iodine liberated.				
	A.	B.	C.	D.	E.	A.	B.	C.	D.	E.
10	4.45	6.1	7.2	7.2	8.0	11.1	15.3	18.0	18.0	20.0
20	6.7		11.4	11.5	12.6	16.8		28.5	28.8	31.5
25		10.55					26.4			
30			14.1	14.4				35.3	36.0	
45		14.4					36.0			
50	11.95				19.6	29.9				49.0
55			18.6	19.1				46.5	47.8	
80		18.25		21.6			45.6		54.0	
110			21.15		26.1			52.9		65.3
115	17.3					43.3				
120		20.8					52.0			
160				26.1					65.3	
185			25.45		28.9			63.6		72.3
190	20.1					50.3				
260		25.2		29.15			63.0		72.9	
310	22.5					56.3				
330		26.5					66.3			
360		26.65	28.45		32.1		66.6	71.1		80.3
410	23.9		59.3			59.3				
430		28.3	32.1	32.15	33.15		70.8	80.3	80.4	82.9
530	25.15					62.9				
690		30.5	34.0	34.55	35.3		76.5	85.0	86.4	88.3
780	26.65					66.6				
840		32.0					80.0			
1380	29.2					73.0				
1980	30.4					76.0				

CONCLUSIONS.

The foregoing results lead to the following conclusions:

1. The speed of the reaction is influenced to a marked de-

VI.



gree by the temperature, the speed increasing with rise of temperature.

2. The presence in the mixture of an excess of one or more of the components increases the speed. The effect of an excess of potassium iodide is about the same as an equivalent excess of potassium chlorate. But a corresponding excess of acid causes a greater increase of speed.

3. Other things being equal the speed of the reaction is modified by the degree of concentration of the mixtures, the speed increasing with the concentration.

4. To obtain the complete reduction of potassium chlorate by potassium iodide and hydrochloric acid in a comparatively short time, the solutions must be concentrated, there

must be present quite an excess of both potassium iodide and hydrochloric acid, and the mixture must be strongly heated.

5. The presence of an excess of the ordinary inorganic acids accelerates the reaction. Assuming their respective influences as indicating their relative strengths,[1] the results on acceleration show the following order of strength: (1) hydrobromic, (2) hydrochloric, (3) nitric, and (4) sulphuric.

ON THE EXISTENCE OF THE SULPHOXYANTIMONIATES.

By LeRoy W. McCay.

The recent appearance of Dr. Bohuslav Brauner's paper on the action of hydrogen sulphide on solutions of antimonic acid[2] induces me to publish the following preliminary notice respecting my own work on the same subject.

Rammelsberg's Salt.

In the year 1841, in an article upon the sulphantimoniates and sulpharseniates,[3] Rammelsberg described a remarkable salt which he obtained by treating pentasulphide of antimony with cold, moderately concentrated potassium hydroxide. The potassium metantimoniate which separated out as a heavy white powder on treating the pentasulphide of antimony with potassium hydroxide was removed by filtratation, and the filtrate concentrated by evaporation. The hot liquid thus obtained yielded on cooling long, needle-shaped crystals of a colorless salt which bore no resemblance to the ordinary potassium sulphantimoniate. The following is Rammelsberg's analysis:

Potassium	23.400[4]
Antimony	37.803
Sulphur	18.195
Oxygen	7.298
Water	13.304
	100.000

[1] These acids are arranged in the same order by Ostwald, who investigated the influence of their presence on the speed of the reduction of bromic acid by hydriodic acid: Ztschr. phys. Chem., **2**, 135, (1888.) It was also found that organic acids and boric acid do not increase the speed.

[2] J. Chem. Soc., **67**, 527 (1895). [3] Ann. der Phys. Pogg., **52**, 193.

[4] His second determination of potassium. I take this figure rather than the other (22.60) because it makes the results found agree better with those demanded by theory.

Rammelsberg regarded the compound as a double salt, and wrote its formula $2(K_3SbS_4) + 9H_2O + 2(KSbO_3) + H_2O$. A salt having such a composition would, according to Rammelsberg, require:

Potassium	23.002
Antimony	37.863
Sulphur	18.889
Oxygen	7.043
Water	13.203
	100.000

It will be observed that these percentages agree remarkably well with those found.

The peculiar composition of the salt did not fail to surprise Rammelsberg. In discussing the matter he states definitely that it is, with one exception,[1] the only compound of the kind known to the chemist.

The results of my study of the action of sulphuretted hydrogen on solutions of antimonic acid—a matter which has engaged my attention more or less ever since the appearance of my paper on the action of sulphuretted hydrogen on solutions of arsenic acid[2]—have led me to believe that the salts of sulphoxyantimonic acid are capable of existing. I have felt convinced for a number of years that the formation of the mixture of antimony pentasulphide, antimony trisulphide and sulphur which, under ordinary circumstances, is always formed when sulphuretted hydrogen is permitted to bubble through acidified solutions of antimonic acid, can be explained in a manner perfectly analogous to that in which the mixture of arsenic pentasulphide, arsenic trisulphide and sulphur is accounted for when sulphuretted hydrogen acts on acidified solutions of arsenic acid. A great deal of work, however, satisfied me that it would be impossible to solve the problem by merely considering the products formed during the interaction of the sulphuretted hydrogen and antimonic acid under different circumstances; consequently I decided to make a number of experiments with the view of settling defi-

[1] Berzelius has described a salt of tungsten to which he assigns the formula $K_2WS_4 + K_2WO_4$.—Traité de Chimie, 2 Ed., III, p. 197.

[2] This JOURNAL, 10, 459.

nitely whether the salts of sulphoxyantimonic acid could be prepared.[1] By examining into the properties and reactions I hoped to obtain an insight into the mechanism of the changes which, until recently,[2] have been fully as mysterious as those relating to the interaction of sulphuretted hydrogen and arsenic acid used to be.

It was while endeavoring to prepare the barium salt of monosulphoxyantimonic acid, that I ran across the article of Rammelsberg above referred to. A mere glance at the formula proposed by him for this double salt persuaded me that it was one of the suspected sulphoxyantimoniates—not the particular one I was looking for, but still a sulphoxy compound. It will be seen that the dualistic formula $2(K_3SbS_4) + 9H_2O + 2(KSbO_3) + H_2O$ can be written $K_4Sb_2O_3S_4 + 5H_2O$—*i. e.*, we can regard the compound as a sulphoxy salt of the pyro form. Using the more recent atomic weight determination[3] in the calculation, a salt of this composition would require:

K_4	23.59
Sb_2	36.27
O_3	7.24
S_4	19.33
$5H_2O$	13.57
	100.00

These figures are practically the same as those found by Rammelsberg. But another possibility suggests itself. The Rammelsberg salt can be regarded as a secondary potassium orthodisulphoxyantimoniate, $K_3HSbO_3.S_3 + 2H_2O$. Since the days of dualism are about past, and our modern conceptions concerning the make-up of double salts are quite different from those in vogue when Rammelsberg published his article on the sulphantimoniates and sulpharseniates, the ideas here thrown out would seem to be perfectly reasonable.

Preparation of the Salt.

The matter is one of intense interest, and inasmuch as a proof of the existence of the sulphoxyantimoniates would, as before

[1] According to Feit and Kubierschky the sulphoxyantimoniates are incapable of existing at ordinary temperatures.—Ber. d. chem. Ges., **21**, 1660.

[2] Brauner: *Loc. cit.*

[3] Classen: *Quant. Anal. Chemie*, 3te Aufl. Also Sb = 120.

intimated, serve to cast a great deal of light upon, if not completely account for, the peculiar conduct of antimonic acid when treated with sulphuretted hydrogen, it seemed wise to repeat Rammelsberg's experiments and examine the salt in detail. A revision of his work appears all the more desirable when we consider the fact that over half a century has elapsed since the attention of the chemical world was called to the existence of the salt.

I.—Pentasulphide of antimony, prepared by precipitating a solution of Schlippe's salt with sulphuric acid, was washed, dried, and treated with a sufficient amount of cold, moderately concentrated potassium hydroxide to produce complete decomposition. After standing about twenty-four hours, the dirty, white precipitate of potassium metantimoniate was filtered off, and the filtrate, in a porcelain dish, evaporated on the water-bath until signs of crystallization were observed. The source of heat was now removed, the dish with its contents placed in a cool spot and the crystallization allowed to proceed. In the course of twelve hours there had separated out a number of semispherical aggregates made up of needle-shaped crystals grouped in concentric radiating clusters. The diameters of some of the aggregates were fully one centimeter. The mother-liquor was poured off, and the crystals freed as far as possible from that adhering to them by first bringing them into a large Gooch crucible made of platinum, connecting this in the ordinary way with the water-pump, and sucking them until all spraying at the bottom of the crucible had ceased. They were then pressed again and again between folds of filter paper until they no longer stained the same, and finally dried in a vacuum over caustic lime. They were of a straw-yellow color. The following are the results of my analysis of the salt:

Potassium	23.10	....	....
Antimony	36.97	36.60	....
Oxygen	....	....	....
Sulphur	....	18.64	....
Water	....	....	13.79

The percentages are to all intents and purposes the same as those found by Rammelsberg.

The salt could be kept for a long time in a vacuum over

caustic lime without undergoing decomposition, but in the air, especially when this was moist, the crystals soon became sugar-brown, then red, and finally crimson. They did not, however, deliquesce or crumble to pieces, but apparently remained dry, and, as far as form was concerned, intact. When freshly prepared the salt was completely soluble in water, but when it had become reddish there was always a small residue which refused to dissolve. This residue appeared to be sulphide of antimony.

II.—In order to obtain a larger quantity of the salt, I treated 64 grams of antimony pentasulphide (Golden Sulphur —Merck & Co.) in an Erlenmeyer flask of about 650 cc. capacity, with 46 grams of potassium hydroxide (87.4 per cent. KOH) dissolved in 250 cc. of water. The flask was corked, violently shaken every now and then, and allowed to stand in a cool place for twenty-four hours. The potassium metantimoniate was filtered off, and the reddish filtrate evaporated in a large porcelain dish on the water-bath until signs of crystallization appeared. The source of heat was now removed and the crystallization allowed to proceed on the bath. The yield here was much larger than in the first case. There were no semispherical aggregates formed; the crystals separated out more as individuals, and they were longer and thicker than those first obtained. Some were as long and as thick as an ordinary pin. The mother-liquor was removed and the salt dried as described under I. The above quantities of antimony pentasulphide and potassium hydroxide were used because it seemed probable that the salt might be formed in accordance with the equation

$$2Sb_2S_5 + 9KOH = K_3HSbO_3.S_3 + KSbO_3 + 2K_3SbS_4 + 4H_2O.$$[1]

On concentrating the filtrate a second crop of crystals was obtained.

Analyses.

Potassium	23.01	....	....	....	....
Antimony	36.69	....	36.97	....	....
Oxygen	....	....	....	....	....
Sulphur	....	18.38	....	....	18.57
Water	....	13.27	13.38	13.22	....

[1] $2Sb_2S_5 + 9KOH = 3K_3HSbO_3S_3 + K_3SbS_4 + 3H_2O$. A portion of the salt, however, owing to its instability, decomposes, splitting up into potassium metantimoniate and potassium sulphantimoniate: $2(K_3HSbO_3.S_3) = KSbO_3 + K_3SbS_4 + H_2O$.

Secondary Potassium Orthodisulphoxyantimoniate.

The question now arises, what is this salt? As I have indicated, there are three possibilities. It is either (a) a double salt, (b) pyrosulphoxy salt, or (c) a secondary orthodisulphoxyantimoniate. The chance of its being a double salt in the Rammelsberg sense is extremely improbable, for from our modern standpoint a dualistic conception in regard to the composition of a compound is scarcely permissible when its constitution can be as well expressed by means of a unitary formula. If we define a double salt to be a polybasic acid in which the hydrogen is partly or wholly replaced by equivalent amounts of two metals, the compound in question will be removed at once from the class of double salts. This must be so for the salt contains but one metal. This fact, along with the occurrence together in a compound of an oxy- and sulphoacid of the same element, puzzled Rammelsberg, and he is very careful to point out that, with one possible exception,[1] the phenomenon is unique. Is it a pyrosulphoxy compound? We have no definite means for deciding against this view, but there is no reason why we should assign to the salt the more complex pyro structure when the facts can be equally well accounted for by regarding it as a simple ortho compound. The salt exhibits the characteristics of a sulphantimoniate far more than it does those of an oxyantimoniate. As far as I can discover, no pyrosulphantimoniates have ever been prepared, whereas the ortho compounds are well known; hence it would be gratuitous to write the formula for the salt $K_4Sb_2O_3.S_4 + 5H_2O$. When heated it acts precisely as a secondary salt might be expected to behave. At 110° it loses very little water,—only a few milligrams. When kept, however, for two hours at 150°, four-fifths of its water escapes. At 250–260° the last traces are evolved and the salt is yellow and anhydrous. As proof of my statement I offer the following determinations of the water in a sample of the salt:

0.8474 gram of salt was kept at a temperature of 145–150° for two hours and then weighed. It was again placed in the air-bath and kept at 145-160° for one and a half hours. The

[1] Berzelius' $K_2WO_4 + K_2WS_4$ is undoubtedly a sulphoxytungstate, $K_2WO_2.S_2$. I hope to examine this salt soon.

weight remained constant. The loss amounted to 0.0888 gram = 10.48 per cent. H_2O. It was now heated to 250–260° and kept at this temperature until the weight remained constant. The loss equalled 0.0232 gram = 2.74 per cent. H_2O. 10.48 + 2.74 = 13.22 per cent. H_2O, while theory demands 13.57. The determination was made a second time with 0.8407 gram salt. At 145–150° it lost 10.68 per cent. H_2O; and at 250–260°, 2.70 per cent. H_2O. 10.68 + 2.70 = 13.38 per cent. H_2O.

Assuming then that the water which escapes at 140–150° is water of crystallization, while that evolved at 250–260° is water of constitution, the simplest and most consistent formula we can assign to the compound is unquestionably $K_2HSbO_4.S_2 + 2H_2O$. In other words it is the secondary potassium salt of orthodisulphoxyantimonic acid.[1]

	Calculated for $K_2HSbO_4.S_2 + 2H_2O$.		Found.				
K_2	78.06	23.59	23.01	....	....	....	....
H	1.00	0.30	....	....	0.30	0.30	....
Sb	120.00	36.27	36.69	36.97	....	....	....
O_4	31.92	9.65	....	....	....	....	....
S_2	63.96	19.33	....	18.38	....	....	18.57
$2H_2O$	35.92	10.86	....	....	10.68	10.48	....
	330.86	100.00					

Reactions.

The hydroxides of the alkaline earth metals produce in aqueous solutions of the salt white precipitates which on standing become crystalline. Silver nitrate gives a jet black, copper sulphate a dark red, and lead acetate a cherry-red precipitate. The latter two precipitates become black on standing. The precipitates do not appear to be sulphoxy compounds. If an aqueous solution of the salt be treated with a few drops of acetic acid a very small amount of sulphuretted hydrogen is evolved; the liquid becomes orange in color, but it remains perfectly clear for days. If the flask containing the solution be corked immediately after the addition of the acid, and well shaken, the sulphuretted hydrogen evolved is soon absorbed, and so completely that the atmosphere of the

[1] K. Preis has prepared the tertiary sodium salt of orthodisulphoxyarsenic acid, $Na_3AsO_3.S_3 + 10H_2O$. Ann. Chem. (Liebig), **257**, 184.

flask is without action on acetate-of-lead paper. When hydrochloric acid is added to a solution of the salt, a mixture of antimony pentasulphide, antimony trisulphide and free sulphur, along with some antimony pentoxide and antimony trioxide is precipitated, while small amounts of antimony pentoxide and antimony trioxide remain in solution. The more acid is added, care being taken not to add enough to attack the sulphides, the more pentoxide and trioxide remain dissolved. In this case also traces of sulphuretted hydrogen escape, but if the experiment be conducted in a closed flask which is occasionally well shaken the gas is after a short time completely absorbed.

In my qualitative study of the action of acids on solutions of the salt, I proceeded as follows: The salt (about one gram) was placed in a small flask, dissolved in water (100 cc.), hydrochloric acid (5–10 cc.) added, and the flask corked and violently shaken. After standing until the supernatant liquid was clear, the red precipitate was filtered off, washed thoroughly with water to remove the hydrochloric acid, and then again and again with alcohol and carbon bisulphide. The alcohol and carbon bisulphide washings were collected separately and evaporated. A residue of sulphur remained. The red precipitate, now free from sulphur, was extracted with a strong solution of tartaric acid and then washed with water to remove this. The tartaric-acid extract proved on further examination to contain considerable quantities of the pentoxide and trioxide. Since relatively large amounts of sulphur were removed by the alcohol and carbon bisulphide, the red precipitate must of course have contained antimony trisulphide. The fact that the red precipitate after the various washings always dissolved in strong hydrochloric acid with separation of sulphur proved that it also contained antimony pentasulphide. One part of the original filtrate from the red precipitate was tested for antimony pentoxide with potassium iodide, according to Bunsen's method. On the addition of a few crystals of this salt to the liquid it became reddish-brown. To the other portion silver nitrate[1] in excess was added, then

[1] In making this test of Rose, the formation of silver chloride does not seem to interfere in the least with the reaction, provided one uses enough of the reagents—especially of ammonia.

potassium hydroxide and finally ammonia. A heavy black precipitate insoluble in ammonia separated out, showing the presence of antimony trioxide. The sulphoxyantimonic acid then, set free upon the addition of a mineral acid to an aqueous solution of the Rammelsberg salt, undergoes decomposition at once, and apparently according to the following scheme:

$$8H_3SbO_3S_3 + 12H_2O = Sb_2S_3 + 2Sb_2S_5 + 5S + H_3SbO_4 + H_3SbO_3 + 21H_2O.^1$$

Of course a great deal will depend upon the strength of the salt solution, the concentration of the mineral acid, and the temperature, but the equation will serve to give a fair idea of the reaction. The presence of antimony pentoxide in the red precipitate and in the filtrate from it is a matter in regard to which I am not quite clear. Judging from what occurs in the corresponding case of the sulphoxy compounds of arsenic, one would expect only a separation of the trioxide.[2] I am devoting much time to a study of this remarkable reaction, and will reserve a further discussion of it for a future time when I hope to publish the results of my examination of the action of sulphuretted hydrogen on acid solutions of antimonic acid. In the light of the elaborate and excellent work recently done by Dr. Brauner and that shed on the subject by the above considerations in regard to the existence of the sulphoxyantimoniates, the action of sulphuretted hydrogen on antimonic acid solutions can no longer be regarded as a mystery.

[1] I venture to predict that the orthodisulphoxyantimonic acid first splits up into orthomonosulphoxyantimonic acid and sulphuretted hydrogen, and that it is owing to the interaction of these two compounds along with water that the complex mixture of sulphides, oxides and sulphur is due: $8H_3SbO_3.S_2 + 12H_2O = 8H_3SbO_3.S + 8H_2S + 4H_2O$.

[2] Michaelis, however, has proven that orthomonosulphoxyphosphoric acid splits up as follows: (1) $H_3PO_3.S + H_2O = H_3PO_4 + H_2S$, and (2) $H_3PO_3.S = H_3PO_3 + S$.—Ber. d. chem. Ges., **5**, 4.

PRINCETON, NEW JERSEY, AUGUST, 1895.

Contribution from the Laboratory of General Chemistry of the University of Michigan.

TETRINIC ACID.

By Paul C. Freer.

A paper on the constitution of tetrinic acid by Louis Wolff[1] has just appeared, and in it the author reaches the conclusion that the acid is a lactone having the structure

$$CH_3.CO.\underset{\llcorner\!\!\!

Wolff's work is there any direct proof of the simpler formula $C_5H_4O_3$ of tetrinic acid, yet when we consider the peculiarities of tetrinic acid (such as its high melting and boiling-points), it is evident that the true molecular weight should be definitely settled, before the decomposition products of the acid can be regarded in their proper aspect. If tetrinic acid were to have a lactide formula similar to that suggested by Nef, it is very easily conceivable that the various reagents used to decompose the same would give bodies which would equally well agree with this or with the simpler lactone constitution. In many respects tetrinic acid is a most peculiar body, whose properties are entirely at variance with what we should expect those of a substance of the structure

$$\underline{CH_2.CO.CH(CH_3)CO.O}$$

to be. Especially prominent are the intensely acid properties which are made apparent by Walden[1] in his study of the electric conductivity of solutions of tetrinate of sodium, for he found the avidity of tetrinic acid to be five times that of the monobasic fatty acids, and besides, it is a well known fact that tetrinic acid easily decomposes carbonates. Such properties are not, however, those of ordinary ketones. They would be more intelligible were tetrinic acid to possess the formula

$$\underline{CH_2.C(OH) : C(CH_3).CO.O}$$

which was assigned to it by me[2], or if it were to have that given it by Nef[3] or originally by Wolff.[4]

Because of these contradictory properties, and also, if possible, to strengthen my former views, I have from time to time continued my investigation of tetrinic acid and, as a result, I can come to no other conclusion than that at which I originally arrived. Owing to the recent paper by Wolff, I have decided to publish the results which I now have, and then to leave the field to my German colleague. I have the more right to do so, as my conclusions differ from his, and as none of my work has been parallel or in contact with his own.

In studying the structure of tetrinic acid, it is of primary

[1] Ber. d. chem. Ges., **24**, 2029. [2] This JOURNAL, **13**, 311.
[3] Ann. Chem. (Liebig), **266**, 92. [4] *Ibid.*, **260**, 87.

importance thoroughly to understand the chemical nature of the monobrom derivatives of methyl acetoacetic ester. Nef[1] maintains that brommethylacetoacetic ester is an α-substitution-product because, by the action of bromine on sodium methylacetoacetic ester or on the free substance, he has obtained an oil which boils constantly at 107° (30 mm.), which gives analytical results in accord with theory, does not dissolve in aqueous alkalies, is not changed by cold nitric acid, and which, he says, changes to tetrinic acid and ethyl bromide, quantitatively on heating for six hours at 100°. Basing his views on the supposition that here there is in reality α-brommethylacetoacetic ester, he maintains that the only possible formula for tetrinic acid is either

(1) $CH_3.CO.C(CH_3).CO$ or (2)

$$CH_2=C(OH)-C(CH_3)<\begin{matrix}O-CO\\CO-O\end{matrix}>C(CH_3)-C(OH)=CH_2$$

and of these he favors the latter.

Wolff has in his recent article shown beyond a doubt that tetrinic acid is really a γ-lactone, or a derivative, for he obtained $C_2H_5.CO.CH_2OH$, (ethyl ketol) and glycolic and propionic acids as decomposition products on heating with water and baryta respectively, and in addition reduced the anilide of tetrinic acid to phenylamidoα-methylbutyrolactone.

This author, however, does not doubt that α-brommethylacetoacetic ester is the original source of the acid, and explains its formation by assuming a molecular rearrangement before the separation of ethyl bromide, such as Hantzsch[2] has shown to be the case with α-bromacetoacetic ester under the influence of hydrobromic acid.

The Action of Bromine on Methylacetoacetic Ester and its Sodium Derivative.

I have subjected the action of bromine on methylacetoacetic ester to a careful revision, and have come to conclusions which differ from those of Nef in many particulars. In his paper[3] Nef says that on treating sodium methylacetoacetic ester with one molecule of bromine, no trace of hydrobro-

[1] Ann. Chem. (Liebig), **266**, 90. [2] Ber. d. chem. Ges., **27**, 3168.
[3] Ann. Chem. (Liebig), **266**, 62.

mic acid is developed, as is the case with sodium acetoacetic ester. If this is so, the resulting monobrommethylacetoacetic ester would necessarily have to be an α-substituted product, as the following reaction will show:

$$\text{I.—}CH_3.CONa : C(CH_3)COOC_2H_5 + 2Br =$$
$$CH_3.CONa.\underset{Br}{C}.CH_3.COOC_2H_5.$$
$$\text{II.—}CH_3.CONa.\underset{Br}{C}(CH_3)COOC_2H_5 =$$
$$CH_3.CO.\underset{Br}{C}(CH_3)COOC_2H_5 + NaBr.$$

If, on the other hand, it can be shown that hydrobromic acid really is developed, then it is equally certain that a γ-product must at least in part be obtained. If, now, sodium methylacetoacetic ester, suspended in absolute ether, is treated with one-half the calculated quantity of bromine, there is found in the etherial solution separated by filtration an oil which consists mainly of free methylacetoacetic ester, mixed with a minor quantity of the brominated product,[1] while a considerable quantity of tetrinic acid, in a very impure state, is left in the retort after distillation. On the other hand, if one molecule of bromine is used, there results a product which contains no unchanged methylacetoacetic ester, but which distils much as Nef describes with the exception that the product has no absolutely constant boiling-point, and leaves a considerable residue of impure tetrinic acid. The formation of free methylacetoacetic ester, however, shows that hydrobromic acid must have been present during the first part of the reaction, and that as a consequence γ-methylacetoacetic ester must, at least in part, have been formed. The action of bromine on sodium methylacetoacetic ester must therefore have been partly one of direct substitution, with separation of hydrobromic acid, as follows:

[1] From 72 grams of Kahlbaum's methylacetoacetic ester, the sodium derivative of which I prepared according to Nef's directions, I obtained 26 grams of fractioned methylacetoacetic ester (B. P., 88–91°; 30 mm.), which I afterward brominated and converted into tetrinic acid. From a second sample (48 grams) of pure methylacetoacetic ester, prepared by myself, I regained 8 grams of impure methylacetoacetic ester—a relatively smaller quantity than the above—and in this case I obtained no residue of tetrinic acid. This experiment will be described further on.

$$CH_3.CONa : C(CH_3).COOC_2H_5 + 2Br = CH_2Br.CONa.C(CH_3).COOC_2H_5 + HBr.$$

$$CH_3.CONa : C(CH_3).COOC_2H_5 + HBr = CH_3.COH : C(CH_3).COOC_2H_5 + NaBr.$$

In brominating free methylacetoacetic ester I have come upon remarkable results. I carefully purified a sample which I had obtained from Kahlbaum by shaking several times with a dilute sodium-hydroxide solution, drying and then fractioning into two portions, one boiling at 84–85° (25 mm.) and the other 85–87° (25 mm.). 11 grams of the 84–85° body was dissolved in 3 volumes of pure chloroform, cooled with ice-water and then brominated with the calculated quantity (15.5 grams) of bromine. The chloroform and hydrobromic acid were then evaporated in the cold in a vacuum, and the resulting oil fractioned. The greater part passed over between 107° and 112° (30 mm.), and there remained 1.1 grams of tetrinic acid in the flask. I could obtain no perfectly constant body from the oil, but the portion boiling between 107° and 112° (30 mm.) gave analytical results agreeing with monobrommethylacetoacetic ester. Quite different results were obtained from the methylacetoacetic ester which passed over between 85° and 87°. Of this substance I brominated 11 grams in the same way, and after removing chloroform and hydrobromic acid as before, I fractioned at 30 mm. pressure. When the temperature of the oil-bath had reached 120°, the pressure suddenly fell to 70 mm., a violent ebullition of ethyl bromide took place and the contents of the flask became solid. The distillation was carried on until the oil-bath reached 142°, when one-third had passed over, and partly solidified in the receiver. The remainder in the flask consisted of 4 grams of pure tetrinic acid. On brominating 56 grams of the Kahlbaum ester, which had not been separated by fractionation, a similar result was obtained. When the oil-bath was heated to 100°, 30 mm. pressure, nothing but a little chloroform and ethyl bromide had passed off. The pressure then suddenly sank to 100 mm., a violent ebullition of ethyl bromide took place, and the contents of the distilling-flask solidified, yielding 13 grams of pure tetrinic acid. This was filtered off and the mother-liquors were then fractioned, when they passed over between

107° and 110° without forming any more tetrinic acid. As all of these results were obtained under the same conditions, I came to the conclusion that the difference lay in a difference between the two fractions of methylacetoacetic ether (84–85° and 85–87°, 25 mm.). I therefore prepared 250 grams of methylacetoacetic ester in the laboratory, taking every precaution to obtain a pure product, and removing any unchanged acetoacetic ester by extraction with dilute sodium hydroxide. This product I carefully fractioned and separated into two portions, one boiling constantly at 107° (49–50 mm.), and the other which consisted only of about 30 grams, between 108 and 109° (50 mm.). 60 grams of the first product were dissolved in 5 volumes of chloroform, placed in a freezing-mixture and the calculated quantity of bromine, dissolved in chloroform, slowly added under constant stirring. The resulting solution was shaken with water to remove hydrobromic acid, dried over calcium chloride, and the chloroform then removed at 30° by distilling under reduced pressure. The remaining colorless oil was then fractioned under 30 mm. pressure. The entire substance, excepting 5 grams, then passed over between 107° and 111°, and no tetrinic acid was left in the retort. This result was therefore radically different from that obtained with the Kahlbaum methylacetoacetic ester, and a repetition brought about the same result. The major portion of the oil (54.1 grams) distilled between 107° and 109° (30 mm.), and a lesser amount (7 grams) between 109° and 111°, while 5 grams went over between 111° and 120°. The bromination-product has not, therefore, an absolutely constant boiling-point. The product (107–109°) on refractioning also separates into a higher and lower fraction. I have never obtained the oil which Nef describes, boiling constantly at 107° (30 mm.), although I took every precaution to have a constant boiling methylacetoacetic ester and varied the bromination in every way. Bromine determinations of each fraction, beginning with the lowest, show a steadily increasing amount of bromine from 26.5 per cent. up, but never exceed the quantity calculated for monobrommethylacetoacetic ester, in fractions below 111°. The result is scarcely different if the methylacetoacetic ester is brominated at ordinary temperatures, and if

the hydrobromic acid is removed by evaporation in a vacuum, although in the latter event more high-boiling oil and some tetrinic acid are obtained on distillation. There is, therefore, a radical difference between the behavior of the Kahlbaum methylacetoacetic ether and that prepared by the usual method in the laboratory, the one promptly yielding a large quantity of tetrinic acid when the distilling flask is heated to 100°, while the other distils with but little decomposition. In no event, however, is an absolutely constant-boiling oil obtained. A very large proportion, it is true, passes over between 107° and 109°, with the thermometer remaining stationary for some time at 108.5° (30 mm.)[1], but a considerable part of the bromination-product boils from 109 to 111°, and another part from 111° to 125°, the high-boiling residue passing over up to 150°. The high-boiling fractions (125–145°) contain more bromine[2] than is required for monobrommethylacetoacetic ester, and hence consists largely of dibrommethylacetoacetic ester. Some unchanged methylacetoacetic ester passes over below 100°, showing that a portion of the bromine is used to form the dibrom product. In brominating methylacetoacetic ester, with the calculated quantity of bromine, therefore, a portion of the bromine attacks the ester, which is already substituted, while a part of the substance remains unaffected.

The product boiling at 107.5° to 108.5°, as indeed is true of all of the fractions, is instantly attacked by pure bromine (free from hydrobromic acid), if it is not diluted; if, however, it is mixed with five times its volume of pure chloroform, the action of bromine is extremely slow; one drop of bromine, added to five grams so diluted, remains unchanged for several hours, but if the mixture is allowed to stand over night, bromination takes place, until finally the calculated quantity for the formation of a dibrom product can be added. The resulting colorless oil, when washed with water, dried over calcium chloride and distilled, boils at 144° (25 mm.), and is undoubtedly dibrommethylacetoacetic ester.

[1] I was very careful to use an absolutely correct manometer, the pressure in which and in all subsequent distillations, unless otherwise stated, was kept constantly at 30 mm. The thermometer in the distilling-flask was entirely in the vapor of the distillate and the oil-bath was kept constant at 128°.

[2] An analysis of this portion shows 45.66 per cent. bromine, calculated for dibrommethylacetoacetic ester, 52.9 per cent.

The Action of Sodium on Monobrommethylacetoacetic Ester.

30 grams of monobrommethylacetoacetic ester were dissolved in 8 times the volume of absolute ether, and then the calculated quantity of sodium (3.1 grams) in the form of fine wire was added. A reaction, *accompanied by the evolution of hydrogen*, at once set in, increasing in violence so that the flask had to be kept cool. After two hours all of the sodium had disappeared, the solution had become brown in color, and a brownish yellow precipitate had separated. The precipitate was removed by filtration. It had an alkaline reaction when added to water,[1] and on acidifying a brown oil separated. The filtrate was also acidified, washed with water and dried over calcium chloride. The two products were then fractioned separately, under 30 mm. pressure, but gave substantially the same result. About one-third passed over below 90°, and consisted of regenerated methylacetoacetic ester; the next portion, less in quantity, contained unchanged brommethylacetoacetic ester; and after this had passed over the thermometer rapidly rose to 200°, and a thick oil distilled which could not be crystallized, and from which no constant boiling product could be obtained. It is neutral and colors a solution of ferric chloride a deep red. Probably this substance is related to succinylosuccinic ester, but its small yield and uninviting properties caused me to forego further investigation. The formation of hydrogen by the action of sodium shows that γ-brommethylacetoacetic ester must have been present.

Oxidation of Brommethylacetoacetic Ester.

Brommethylacetoacetic ester, when covered with a dilute solution of sodium carbonate is instantly oxidized by a solution of potassium permanganate. 19 grams of brommethylacetoacetic ester (boiling-point 108.5°) was mixed with a solution of 9 grams of sodium carbonate in 150 cc. of water, and then 20 grams of potassium permanganate, dissolved in one liter of water, was slowly added, with constant stirring. When the reaction was complete the manganese dioxide was filtered out and the whole evaporated to dryness. The salts which remained were then repeatedly extracted with hot alcohol,

[1] The precipitate contains a considerable quantity of sodium bromide.

and the alcoholic solution evaporated. Both the undissolved and the dissolved salts were separately examined. The result was that the undissolved portion contained sodium oxalate. Now, if we compare the formulae of the γ- and α-brommethylacetoacetic ester—

(γ) $CH_3Br.C(OH):C(CH_3).COOC_2H_5$, and

(α) $CH_3.CO.CBr(CH_3).COOC_2H_5$

—it is evident that oxalic acid can be produced only by the former, which primarily should give bromacetic acid or glycolic acid, which, owing to the ease with which it is oxidized, would subsequently change to oxalic acid. From the α-brom ester, on the other hand, only acetic acid could be expected. The brommethylacetoacetic ester under investigation, therefore contained γ-brommethylacetoacetic ester.

The portion of the salts produced by oxidation, and which was soluble in alcohol consisted mainly of acetate of sodium, mixed with very little carbonate. This mixture was boiled with a little animal charcoal, filtered and the filtrate treated with a solution of lead acetate. A flocculent precipitate is formed, which soon becomes white and crystalline. This precipitate was carefully separated, washed with water and then decomposed with the aid of hydrogen sulphide. The solution, after filtering out the lead sulphide, was evaporated; a crystalline acid remained, which was very soluble in water and alcohol, which contained halogen, and which in its properties resembled monobromacetic acid. The quantity of this substance was too small for exact identification, but when added to that of the oxalic acid it showed that 1.2 grams of the original brommethylacetoacetic ester must have been the γ-brom derivative. This amounts to about 6 per cent. of the original oil. In order to determine whether the sodium derivative of the methylacetoacetic ester prepared by me behaved like that from the Kahlbaum preparation, I repeated the previous experiment in which I used one-half the calculated quantity of bromine. 48 grams of pure methylacetoacetic ester (B. P. 107.5° at 50 mm.) was converted into the sodium derivative by means of sodium in slight excess, and then carefully brominated with 26.6 grams of bromine. The solid product was then filtered out and washed with pure ether, and

both the ethereal solution and the oil obtained by acidifying the solid were worked up separately. The result was different to some extent from the action on the Kahlbaum product, for, whereas in the former case I obtained on fractioning, a considerable quantity of tetrinic acid in an impure state, in this experiment the oil, both from the ether solution and from the acidified solid boiled with but little residue. The ethereal solution gave an oil which was colorless and all of which passed over between 85° and 111° (30 mm.). On refractioning, I isolated 6 grams below 100°, consisting mainly of regenerated methylacetoacetic ester; 9 grams from 100° to 105°, consisting of a mixture of methylacetoacetic ester and brommethylacetoacetic ester; 9 grams from 105° to 107°; 5 grams from 107° to 108°, and 2 grams from 109° to 111°. These results show that there is present a mixture, but that approximately 6 grams of free methylacetoacetic ester were regained. The previous work with the Kahlbaum ester is therefore confirmed, only the product prepared by me gives relatively much less free methylacetoacetic ester, and hence less of γ-brommethylacetoacetic ester.

The solid which was left after brominating sodium methylacetoacetic ester and which was separated from the etherial solution by filtration, was acidified, the resulting oil washed with water, dried and fractioned. It was mainly methylacetoacetic ester (12.5 grams) and a little brommethylacetoacetic ester (1.5 grams). As will be seen, much less than one-half of the methylacetoacetic ester originally used was regained from the solid products of the reaction, although only one-half the calculated quantity of bromine was used in bromination. If the change had taken place entirely according to Nef's view, and no γ-brommethylacetoacetic ester had been formed, then exactly one-half of the methylacetoacetic ester would have been recovered. The loss is accounted for by the fact that the bromine in part substitutes hydrogen in sodium methylacetoacetic ester,[1] that the resulting hydrobro-

[1] It seems probable, from the investigations going on in my laboratory, that the halogens are often capable of directly substituting hydrogen in sodium derivatives, and that the reactions do not always take place by previous addition, with subsequent separation of halhydric acid or metallic halides. The direct substitution of halogen for metal is probably of rare occurrence. Very possibly the production of

mic acid then attacks the sodium methylacetoacetic ester, forming the free compound, while it does not so readily act on the sodium brommethylacetoacetic ester. Sodium brommethylacetoacetic ester does not remain as such, but decomposes and is consequently not regained from the solid product of the reaction, which therefore consists of only one-fourth of the sodium methylacetoacetic ester originally used. A considerable quantity of the brom derivatives must also be found to be present in the ethereal solution which is separated from the solid by filtration for, if the entire reaction were to produce γ-brommethylacetoacetic ester, then there would be enough hydrobromic acid produced to liberate exactly one-half of the methylacetoacetic ester, which latter body would then constitute the entire product to be obtained from the ethereal solution.

Separation of the Brommethylacetoacetic Esters by Alkalies.

As a final proof that the brommethylacetoacetic ester, obtained by direct bromination of pure methylacetoacetic ester is a mixture of α- and γ-brom derivatives, I have extracted an etherial solution of the pure substance of Nef (boiling at 107–108°, 30 mm.) with 10 per cent. caustic soda solution, and instantly neutralized the alkali with sulphuric acid. Under these circumstances an oil separates from the alkaline solution, having the properties of brommethylacetoacetic ether, but which, on distillation, gives a higher-boiling product and a considerable residue in the flask. To my surprise, the portion of the oil which was insoluble in alkalies, and which I took to be pure α-brommethylacetoacetic ester, now had a lower boiling-point by two degrees than it had before, and was not perfectly constant. This oil, insoluble in alkali, and which presumably contained only the α-brom product, I carefully fractioned into portions 100°–104°, 104°–107°, and 107°–109°, and heated each portion separately in a sealed tube at 100° for six hours.[1] There was absolutely no change and no

sodium hypochlorite from chlorine and sodium hydroxide is a reaction involving direct substitution, thus:

$$NaOH + Cl_2 = NaOCl + HCl, \text{ and } NaOH + HCl = NaCl + H_2O.$$

We are at present investigating the action of bromine on sodium phenols, and on sodium ethylate.

[1] The fraction 107–109° (nearly pure α-brommethylacetoacetic ester, *did not change in the least* when heated for ten hours. Then the sealed tube was opened and a little dry, gaseous hydrobromic acid added. The oil then solidified completely to tetrinic acid on heating to 100° in a sealed tube for twenty minutes.

tetrinic acid was formed. On the other hand, brommethylacetoacetic ester which has not been extracted with alkalies, yields tetrinic acid with more or less readiness under these circumstances. In no event, however, is the yield a quantitative one; thus 12 grams of brommethylacetoacetic ester (boiling-point 107–109°), heated for ten hours at 100°, yielded 2.2 grams of pure tetrinic acid. The mother-liquors, on again heating, gave after six hours 0.3 gram more. On fractioning the residue, it boiled as before between 109° and 111°, with a small portion of a high-boiling residue. The mother-liquor from any of the sealed tubes in which tetrinic acid has been formed on washing with water, before fractioning, give a reaction for hydrobromic acid in the aqueous solution. I also found that brommethylacetoacetic ester, to which I had added some dry hydrobromic acid, was changed into tetrinic acid in a very short time. Brommethylacetoacetic ester also absorbs dry hydrobromic acid very readily. The conclusions which can be drawn from this work are as follows:

1. The product of brominating either methylacetoacetic ester or sodium methylacetoacetic ester with the calculated quantity of bromine is not a uniform body. It consists partly of free methylacetoacetic ester, of α- and of γ-brommethylacetic ester and of dibrommethylacetoacetic ester.

2. Tetrinic acid is quickly formed from γ-brommethylacetoacetic ester, so that the latter cannot be distilled without change.

3. α-Brommethylacetoacetic ester does not change to tetrinic acid when heated to 100° unless hydrobromic acid is present, the hydrobromic acid causing the change by addition.

4. There is a difference between different samples of apparently equally pure methylacetoacetic ester when brominated.[1] I can see no other reason for this difference in behavior than

[1] It is possible, also, that the Kahlbaum ester contains methylacetoacetic methyl ester, which might in part account for the difference between it and my body, yet the quantity of this could scarcely be sufficient to account for all of the tetrinic acid formed from it when its bromine derivative is distilled and, besides, the *higher-boiling* fraction gave relatively the most tetrinic acid when distilled. My acetoacetic ester was pure, for it had an absolutely constant boiling-poin . Yet it also gave a brom derivative which, before extracting with alkalies, yielded tetrinic acid on heating to 100°. It would be interesting to repeat the above work, using methylacetoacetic methyl ester.

in the fact that there are two methylacetoacetic esters which are geometrical isomers, *i. e.*—

$$\text{I.}\quad \begin{matrix} CH_3-C.OH \\ \| \\ COOR.C.CH_3 \end{matrix} \qquad \text{and} \qquad \text{II.}\quad \begin{matrix} CH_3.C.OH \\ \| \\ CH_3.C.COOR \end{matrix}$$

Formula I would give a γ-brom derivative of the formula $\begin{matrix} CH_2Br.C.OH \\ \| \\ COOR.C.CH_3 \end{matrix}$, which would readily separate ethyl bromide and go over into tetrinic acid. This body would therefore be present in the brommethylacetoacetic ester which changes so readily into tetrinic acid at 100° on distillation; the other γ-brom body, $\begin{matrix} CH_2Br.C.OH \\ \| \\ CH_3.C.COOR \end{matrix}$ would only change gradually through molecular rearrangement. Finally, α-brommethylacetoacetic ester will not produce tetrinic acid at all unless some means are provided to change it first into the γ-brom.[1] This means is found in the action of hydrobromic acid, just as Hantzsch has shown to be the case with α-bromacetoacetic ester. This change, which actually takes place, could easily be explained if α-brommethylacetoacetic ester were to have the formula $CH_3 : C(OH).CBr(CH_3).COOC_2H_5$, for then it would, on addition of hydrobromic acid, be changed into an addition-product having the structure

$$CH_2Br.CH(OH).CBr(CH_3).COOC_2H_5,$$

which latter body, by separation of hydrobromic acid, would be converted into γ-brommethylacetoacetic ester. However, were α-brommethylacetoacetic ester to have the above structure, it is not easy to see why it does not dissolve in alkalies. It is true that methylacetoacetic ester itself does not dissolve in aqueous alkalies, but one would expect the bromine derivative to be more negative and hence at least as soluble as acetoacetic ester. It must, however, be acknowledged that there are no data at hand to prove that the brom deriva-

[1] The least trace of hydrobromic acid is sufficient to inaugurate the change, which then goes on by separation of hydrobromic acid. In almost all cases unless care has been taken to extract with alkalies, such a trace of hydrobromic acid is present. At temperatures higher than 100° it is formed even from the pure product, and then the production of tetrinic acid goes on.

tive should, of necessity, be any more soluble than methyl-acetoacetic ester itself.

In conclusion, I wish to thank Mr. J. E. Whitsit for his conscientious and active assistance in this research.

DERIVATIVES OF TETRINIC ACID.

Experimental work by E. R. Miller.

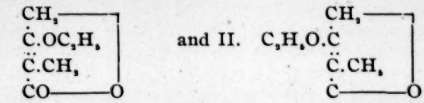
In his recent paper[1] Wolff has investigated a number of decomposition-products of tetrinic acid, produced by the action of water, nitrous anhydride, nitrous acid, and aniline. He comes to the conclusion that the structure of the body is represented by the formula

$$\underset{\llcorner\!\!\!

anhydride, readily yields an acetyl derivative, which dissolves slowly in aqueous potassium hydrate, and from this solution tetrinic acid separates on acidifying, and it will be shown below that similar properties belong to benzoyl tetrinate. Lastly, when we take the stability of sodium tetrinate and its electric conductivity into consideration, there seems to be no doubt as to the hydroxyl group.

One thing still seemed to be necessary in studying tetrinic acid, and that was the definite proof by several methods, that the acid really has the molecular weight assigned to it, and not a double one, as is assumed by Nef, and it was with the object of deciding this point that the investigation of tetrinic acid, begun by Freer, was resumed.

Ethyl Tetrinate.—Tetrinate of silver is, contrary to Demarcay's account, rather soluble in water. A very concentrated neutral solution of potassium tetrinate was precipitated with a concentrated solution of silver nitrate, the precipitated salt filtered, dried on a porous plate, and washed by rubbing in a mortar with water and again filtering,[1] it was finally dried on a porous plate in a vacuum. The resulting perfectly white compound was placed in sealed tubes with one and one-half times the calculated quantity of ethyl iodide and an equal volume of absolute ether. The reaction began in the cold and was finally completed at 80°. The contents of the tube were then filtered and the oil fractioned. By this means, it could be separated into two fractions, one at 175–176° (50 mm.), and the other at 180° (43 mm.) The first fraction remains liquid, but the other becomes solid, melting at 28°. Both the solid and the liquid gave analytical results agreeing with ethyl tetrinate and in accordance with those given by Freer. It seems not improbable that we have here two geometric isomers:



[1] The silver salt must be dried quickly and protected from light, it must not be brought in contact with filter-paper or other organic material, otherwise it rapidly blackens.

but as all attempts definitely to isolate two tetrinic acids have failed, this view is advanced with due caution.

A determination of the vapor-density of ethyl tetrinate was made under diminished pressure (8 mm.) in a large bulb such as is used in the Dumas method, and the result (at 174°) gave for the molecular weight 138.6, calculated 142. There can be no doubt, therefore, that ethyl tetrinate has not a double molecule.

Benzoyl Tetrinate.—20 grams of sodium tetrinate were finely powdered and suspended in 20 cc. of absolute ether, the calculated quantity of benzoyl chloride was then added, and the whole warmed on a water-bath until the odor of benzoyl chloride had disappeared. The ether was then evaporated and the solid residue successively washed with ether, a little alcohol, and finally with water. The resulting benzoyl tetrinate was then dried and recrystallized from pure acetone. It separates in long shiny plates, which melt at 128°. It is slightly soluble in boiling alcohol, being partially decomposed thereby, yielding benzoic ester, and it is also slightly soluble in boiling water.

	Calculated for $C_4H_4O_3C_4H_3CO$.	Found. I.	II.
C	66.05	66.07	65.95
H	4.58	4.9	4.9

The molecular weight was taken in benzene solution[1] according to the Beckmann method:

1. Solvent, 19.4098; substance, 0.0970; depression, 0.11°; $M = 222.6$.

2. Solvent, 21.337; substance, 0.3520; depression, 0.37°; $M = 218.4$.

Calculated $M = 218$. Benzoyl tetrinate has therefore a molecular weight which agrees with theory.

Benzoyl tetrinate is easily saponified by alcoholic potash. 2 grams of benzoyl tetrinate were digested with a slight excess of methyl-alcoholic potash for several hours. After evaporating the alcohol the residue was slightly acidified with diluted sulphuric acid, filtered, and the precipitate washed with water. The wash-water and the filtrate were examined separately. The precipitate was benzoic acid, and the amount agreed with

[1] Glacial acetic acid was tried, but it decomposed the benzoyl tetrinate rapidly.

theory (0.938 gram). The filtrate was evaporated to dryness, extracted with alcohol and the alcoholic solution evaporated. It deposited pure tetrinic acid, 1 gram; theory requires 1.045. Benzoyl tetrinate is, therefore, easily saponified to benzoic and tetrinic acids, one molecule of each. Phosphorus pentachloride decomposes benzoyl tetrinate, yielding benzoyl chloride.

β-Chloroxytiglic Lactone : Tetrinic Chloride.—If tetrinic acid is mixed with the calculated quantity of phosphorus pentachloride and a little chloroform is added, so as to bring the reacting bodies in contact, reaction sets in at once, and there results an oil. The latter was freed from phosphorus oxychloride by distillation under diminished pressure, and a yellowish oil which passed over was washed with water, dried over calcium chloride and fractioned. There results a chlorinated body which boils at 106.5–107.5° at 26 mm. pressure, and the greater portion of which solidifies in a freezing-mixture. The solid crystals were filtered from the oil and recrystallized from ether. They form colorless prisms, melting at 30°. The oily portion, upon repeated fractioning, also in part solidifies and, it was discovered, had the same percentage composition as the crystals. This chlorinated body dissolves slowly on warming with caustic alkalies, and hence has the characteristic property of a lactone. Contrary to Demarcay's description, it is perfectly stable and can be kept any length of time without change.

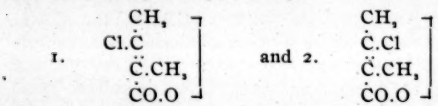
	Calculated for $CH_3.CCl:C(CH_3)CO.O$.	Found. I.	Found. II.
C	45.7	45.39	....
H	3.77	3.87	....
Cl	26.79	....	26.5

These results agree with the calculated amounts for tetrinic chloride. The vapor-density of the body determined in the Hofmann apparatus, in the vapor of xylene, gave for the molecular weight, 133.9; calculated molecular weight, 132.5. There can be no doubt from these results that, in the case of tetrinic chloride, as well as in all previous bodies which were studied, the substance is derived from a tetrinic acid of the formula

$$CH_3.C(OH) : C(CH_3).CO.O$$

In his recent paper, Wolff has stated that tetrinic chloride does not exist. It would seem from the above that this statement must be altered.

It is interesting to observe that in the study of tetrinic chloride conditions have been encountered similar to those observed with the ethyl ether of tetrinic acid, *i. e.*, a solid and a liquid tetrinic chloride are present. It seems not improbable, therefore, that here we have the two geometric isomers which are called for by theory, namely :



It would, therefore, be very desirable if work were undertaken with the purpose of isolating the corresponding tetrinic acids. In concluding, I may add that brommethylacetoacetic ester, on prolonged heating to 110°, may be brought to yield 87.4 per cent. of the theoretical quantity of tetrinic acid. Hydrobromic acid is always developed during the reaction, as can be shown by passing the gases which are given off through a solution of silver nitrate.

REVIEW.

THE PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. A Manual for the Estimation of Soils, Fertilizers and Agricultural Products. For the Use of Analysts, Teachers and Students of Agricultural Chemistry. Volume I.—Soils. By HARVEY W. WILEY, Chemist of the United States Department of Agriculture. Easton, Pa. : Chemical Publishing Co. pp. 607.

Based upon the fundamental relation of the soil toward all agricultural operations, the careful analysis and classification of soils offered, very early in the history of applied chemistry, an alluring prospect of the possibility of estimating the potentiality of a farm with ease and accuracy. The superficial observer might still wonder why the realization of these hopes is so long delayed. But in fact the analysis of soils for any purpose is of rather limited value and the results, however accurate as applying to the particular sample under examination, will admit of only very carefully drawn conclusions and

rarely of general application. Nevertheless the attention paid to the methods of soil examination is not inconsiderable and there has of late been much progress in this field, in which American investigators make a creditable showing and are freely quoted.

The volume seems to include about all that has been published on the subject of soils of late years. This feature of the work characterizes it to the extent of frequently unduly emphasizing matters of rather secondary importance which may have been much discussed or written about. Soil geology, soil physics, and soil chemistry are treated in considerable detail, particularly the last two. After a discussion of the origin of soils, their geologic characters and a description of the chemical elements involved in their composition, the various operations of their physical and chemical examination are fully treated. Often a number of methods and authorities are cited in detail without leaving with the reader any definite idea as to which is to be preferred or employed. The subject is treated compendiously and not selectively, and this is in some sense a disappointment, since one might have expected to profit by the author's extensive experience in this field. The work is an elaborate summing up of the subject, comprehensive and exhaustive—a reference book; but the treatment is not critical nor is it the crystallization which would best serve as a guide to analytical work. This latter aim was doubtless less in the author's mind, and it can be unreservedly said that he has given us a most valuable work which must to a large extent supplant other treatises of the kind.

A work of this extent can hardly be free of minor features susceptible of criticism, but such examples so far as they occur here, are of secondary importance. The statement that "water is the most important of all plant foods" (p. 6) certainly depends for its accuracy upon the point of view. The terms "early truck" and "truck farming" (p. 249) might be obscure to one not familiar with American dialects; while the effect of reading that the "reduction takes place in a copper erlenmeyer" is startling, to say the least. The photomicrographs of calcium sulphate and magnesium silico-fluoride (Figs. 51 and 52) are evidently interchanged.

The sections devoted to chemical analysis are excellent and particular attention is given to the important subject of the origin and estimation of oxidized nitrogen, even the details of the methods of isolation and study of the micro-organisms of the soil being given.

The work is a notable and important addition to soil literature. W. E. S.

OBITUARY NOTICES.

LOUIS PASTEUR.

Pasteur died September 28, near Paris. He was born December 27, 1822, at Dôle. In 1843 he entered the École Normale at Paris, and attended the chemical lectures of Balard and Dumas. In his boyhood he had shown marked skill in drawing, and in the field of chemistry at first took special interest in questions of form such as are presented in the phenomena of crystallization. Towards the end of his student career, he repeated, for the sake of the practice, an experimental investigation of de la Provostaye on the crystalline forms of tartaric and racemic acids and their salts. In the course of this work he made the important discovery that racemic acid can be split into two varieties of tartaric acid by crystallizing its ammonium-sodium salt. One of the acids thus obtained, as is well known, is ordinary tartaric acid; the other is a variety that was up to that time unknown. This discovery furnished the foundation of what has since come to be known as stereochemistry. The relations existing between the two varieties of tartaric acid and racemic acid have been shown to exist in many other cases, and these relations have led to the theory of the asymmetric carbon atom, first suggested by Van't Hoff and by Le Bel.

In 1848 Pasteur was called as physicist to the Lyceum of Dijon, and a few months later he accepted the chair of chemistry in the University of Strasburg. In 1854 he became Dean of the Faculty in Lille, and in 1857 he returned to Paris as Director of the École Normale. In 1862 he became a member of the Institute; in 1881 he was elected to the French Academy. In 1874 the National Assembly voted him an annual pension of 20,000 francs. In 1889 he gave up all his public offices in order to devote himself to the management of the famous Pasteur Institute, which was founded by public subscription.

While at Lille, Pasteur took up the study of alcoholic fermentation. His first article on this subject appeared in 1857. In this he showed that fermentation is directly connected with the life and growth of yeast. From this time on, his attention was given largely to the investigation of phenomena produced by minute organisms. He improved the methods used in the manufacture of wines and beers; he discovered the cause of the disease of the silkworm, which threatened disaster to the silk industry of France; and, as all the world knows, he devised methods for combating a number of diseases, such,

for example, as hydrophobia. Pasteur is in fact the father of modern medicine. The methods that he devised for the prevention of chicken cholera and for the treatment of hydrophobia are the methods that seem to promise most success in dealing with many of the diseases of mankind. I. R.

FELIX HOPPE-SEYLER.

Felix Hoppe-Seyler, renowned not only as a teacher, but also as an investigator in the field of physiological and pathological chemistry, died suddenly August 10, 1895. Although seventy years old, he still retained his vigor and activity as a worker. In 1846 he entered the University of Halle, but shortly afterwards went to Leipsic, where he came in contact with the Weber brothers, Erdmann, Lehmann, and others, all skilled and inspiring instructors, and laid a firm foundation for his future work. The latter part of his student course was spent in Berlin, where he took the degree of Doctor of Medicine in 1850. After practicing medicine for a short time, he was appointed Privatdocent in the University of Greifswald, and two years later returned to Berlin as assistant to Virchow. In 1861 he was appointed to the chair of applied chemistry in the University of Tübingen. He resigned in 1872 to accept the professorship of physiological chemistry in the new University of Strasburg.

Hoppe-Seyler's early researches were upon the structure and composition of connective tissue, his dissertation on the structure of cartilage and on chondrin being shortly followed by articles on bone and teeth.

His most valuable contributions were those to the physiological chemistry of the blood. It was early in these investigations that he discovered the peculiar property which many of the principles of the body possess, of rotating the plane of polarization. In a short paper published in 1857 he gives the results of investigations on the action of carbon dioxide on the blood, and concludes that the action of carbon dioxide on the coloring-matter of the blood renders it incapable of acting as a carrier of oxygen. After the researches of Stokes on the reduction of oxyhaemoglobin, Hoppe-Seyler explained in detail the action of carbon dioxide on blood, and devised a method for detecting blood containing carbon dioxide. Following up the line suggested by the work of Brewster and Herschel on the absorption bands formed in the spectrum of light which had been passed through various gases, Hoppe-Seyler studied the behavior of blood-coloring matter in the spectrum of sunlight, and published his celebrated paper on this subject. He concluded, from the investigation of the

absorption spectrum of blood, that haematin, which had been considered the blood-coloring matter, did not exist as such in the blood, but was formed as a product of decomposition. Stokes afterwards showed that the coloring-matter of blood exists in two states of oxidation, distinguished by difference in color and in the spectrum.

Hoppe-Seyler isolated the blood-coloring matter, and studied its composition, its combinations with oxygen and carbon dioxide, and its decomposition.

Only a slight idea of his energy can be gained from the articles published by him, as a large part of the work done under his direction appeared under the names of his pupils. In 1858 he published his "Handbook of Physiologico-Chemical and Pathologico-Chemical Analysis." This work has passed through six editions, the last having been published in 1893. He also published a "Text-book of Physiological Chemistry," and founded in 1877 the "Zeitschrift für physiologische Chemie," of which he has been the chief editor.

J. E. G.